CARBON

COMPOUNDS

APPLETON

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CHAPTERS

ON THE

CARBON COMPOUNDS:

AN

ELEMENTARY TEXT-BOOK

OF

Organic Chemistry,

BY

JOHN HOWARD APPLETON, A. M.

Professor of Chemistry in Brown University.

AUTHOR OF A SERIES OF CHEMICAL TEXT-BOOKS.

a. W. Palmer.

SECOND EDITION.

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PREFACE.

THIS little volume is the third and last of a series of text-books on *general or descriptive chemistry*, prepared for the use of beginners. The first of the series treats chiefly of non-metals; the second treats of the metals of the chemist; and this one, of carbon compounds.

The carbon compounds are so numerous, and in some cases, so complicated in their structure, that it is impossible to deal with more than a very small portion of them in the few pages allotted to this book. It is hoped, however, that the following pages may serve as a tolerable introduction to the wonderful and fascinating branch to which it relates.

The book is not intended to be used alone; it is expected that the student will do laboratory work in connection with it. While many of the experiments in organic chemistry require complicated apparatus and considerable manipulative skill, there are others that may be performed on a small scale and with simple appliances, by students of limited experience. Such experiments, properly ordered, will serve to illustrate the facts and principles presented in a text-book like the present one, and will add greatly to the interest and satisfaction of pupils studying it.

In preparing this edition the matter of the first edition has been completely rearranged and largely rewritten; moreover, very considerable additions have been made.

BROWN UNIVERSITY, PROVIDENCE, R. I.,
   January, 1896.

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CARBON COMPOUNDS.

CHAPTER I.

ORGANIC AND INORGANIC CHEMISTRY.

Chemists long ago recognized certain differences between the substances found in distinctly animal and vegetable matters, on the one hand, and the substances found in mineral matters, on the other : between those things which constitute organisms like animals and plants, as compared with those of non-living substances like clay, iron-rust, alum, saltpetre, etc.

Animal matters and vegetable matters are the products of bodies possessing organs. Organs are parts having specific functions. Thus the stomach is an organ possessing the function of digestion, and the lungs are organs possessing the function of respiration. Again, the leaves, the flowers, the seeds, the roots, of plants, are separate organs, or possess separate organs, and they perform special and very different functions of the living vegetable to which they belong. *Accordingly, substances derived from vegetables and animals are called organic.* Non-living objects, as rocks and other mineral and earthy substances do not possess organs, and they have long been called inorganic.

This division of matters into organic and inorganic was formerly thought an essential one; it is not now considered so. It is now known that the chemical changes of living animals and plants are governed by the same laws as those prevailing in the changes of rocks and other lifeless forms of matter.

Grounds for Dividing Chemistry into Two Great Departments.

Chemistry is still, however, commonly divided into the two great departments—inorganic chemistry and organic chemistry ; but this division is recognized as a matter of convenience mainly.

Three reasons may be mentioned, why the distinction is still maintained :

First. The number of organic compounds is very great.

Second. These compounds perform varied and important offices in connec-

tion with human beings in their growth and nourishment in health, and in their treatment in illness. Many organic compounds have important applications in the arts.

Third. As will appear hereafter, the processes of analysis, and methods of investigation in organic compounds are slightly different, as a whole, from those that serve for the study of inorganic.

Definitions of Organic Chemistry.

The inorganic and the organic worlds are, however, so closely allied in some respects, and certain of the substances of the one have such close and natural affiliations with those of the other, that it is often found difficult to determine where shall be placed the line of demarcation between these two great natural groups. In fact, chemists have not found the definition, incidentally introduced in the preceding paragraph, sufficiently distinct. To make it more so, organic chemistry has been sometimes called *the chemistry of the carbon compounds.* It has sometimes been called *the chemistry of the hydrocarbons.* Again, the following still more rigid and scientific statement is often employed : organic chemistry includes *those compounds in which the atoms of carbon are directly united either with other atoms of carbon, or with atoms of hydrogen, or with atoms of nitrogen.*

The last three definitions exclude from organic chemistry such animal substances as bone (principally calcium phosphate) and the last two definitions exclude such substances as carbon dioxide, CO_2, and carbon disulphide, CS_2.

Two Classes of Organic Compounds.

There is one distinction between the classes of organic compounds that ought not to be omitted here. The members of the organic family differ very much in their properties, according as they are *crystalline* or *cellular.* Crystalline organic compounds, of which cane sugar may be taken as a familiar and suitable example, are numerous. These compounds are closely allied in some respects to inorganic compounds. They do not seem to have so close a relation to the vital processes as might at first be expected. But those organic compounds that are cellular, such, for example, as the fibre of wood and the fibre of lean meat, are much removed from inorganic bodies, and seem to bear a peculiar and close relation to the vital forces.

Cellular organic compounds are often called *organized ;* crystallic organic compounds are often called *unorganized.*

It is worth while to note that certain mineral matters contain organic compounds. Coal is a mixture of organic substances; so is petroleum.

The Great Number of Organic Compounds.

The vast number of organic compounds is referable to at least four fundamental principles :

First. The chief element, carbon, has a large number of points of attraction — that is, four ; on this account it is capable of attaching to itself by chemical affinity many other atoms.

Second. Carbon atoms are capable of uniting in chains of great length and variety of arrangement. Two methods of arrangement are especially noteworthy ; the one method is that where the chains are *open* — that is, not attached at the ends. The other arrangement is that where the chains are *closed*, the series of atoms of carbon making a sort of ring. An appropriate example of this kind of union is found in the benzene ring or benzene hexagon.

The open chain may be conveniently represented by the left-hand diagram below, and the closed chain, the benzene ring, is often represented by the right-hand diagram below.
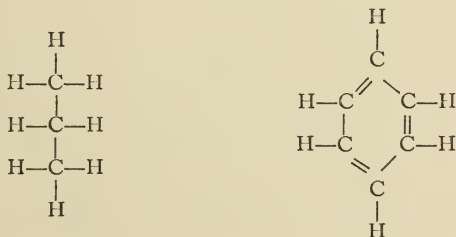
The exact nature of carbon atoms by reason of which they form such chains is not known. It is worthy of note that thus far only two compounds of carbon with *oxygen* are known, carbon monoxide, CO, and carbon dioxide, CO_2. With *hydrogen* alone, on the other hand, carbon forms hundreds of known compounds. Undoubtedly some good reason exists for this great disparity, but it is as yet undetected.

Third. One of the most interesting and important features of organic compounds is that in them certain elements may stay together with considerable stability in comparatively permanent

groups which act like elements.   Such groups of atoms are
called *compound radicles*.

It has already been shown that the number of elements is
about seventy, and that these elements uniting in a variety of
ways form a vast number of compounds.   The organic chemist
has to do not only with the seventy well known elements but
with a vast number of radicles *which act like elements.*   These
radicles, therefore, add very greatly to the capabilities of organic
chemistry.

It is not practicable to attempt here a list of the radicles of organic chemistry.
Many of them will appear in subsequent pages and be readily recognized as
maintaining such integrity through a series of chemical operations as to entitle
them to rank as units comparable to the atoms of the metals and non-metals.
A few very common ones may be mentioned :

$$Methyl, \quad CH_3$$
$$Ethyl, \quad C_2H_5$$
$$Propyl, \quad C_3H_7$$
$$Phenyl, \quad C_6H_5$$
$$Cyanogen, \quad CN$$

A few inorganic radicles are of great importance in organic transforma-
tions, as,

$$Hydroxyl, \quad HO$$
$$Carbonyl, \quad CO$$
$$Carboxyl, \quad COOH$$
$$The\ nitro\ group, \quad NO_2$$
$$The\ nitroso\ group, \quad NO$$
$$The\ amido\ group, \quad NH_2$$
$$The\ imido\ group, \quad NH$$
$$The\ sulpho\ group, \quad SO_2$$
$$The\ thionyl\ group, \quad SO$$
$$The\ sulphonating\ group, \quad HSO_3$$

Fourth.   It is now distinctly recognized that a given organic
compound, possessing a certain distinct set of properties, may
have its atoms undergo a *rearrangement* without any increase in
the number of them or any change in their kinds or relative pro-
portions.

Some organic substances have molecules capable of several dif-
ferent rearrangements, such that several different compounds
may be produced.   Thus Professor Cayley has computed that a
compound of the paraffin group containing four carbon atoms is

capable of two rearrangements within the molecule; but a compound of this group containing thirteen carbon atoms is capable of as many as seven hundred and ninety-nine different rearrangements of its atoms.* This property of organic compounds is called *isomerism.*

In other words, *two or more substances having the same percentage of carbon, hydrogen, and, it may be, of other elements, may have different properties.*

There are several different kinds of isomerism which are worthy of explanation. Such are true isomerism, polymerism, metamerism, geometrical isomerism, etc.

I. Two or more compounds are *truly isomeric* when they have the same elements united in the same percentage proportions and with the same number of atoms in the molecule — but differ in the arrangement of these atoms. The following may serve as examples:

Three Strictly Isomeric Compounds.
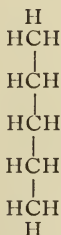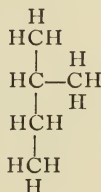
Normal pentane.   Isopentane.   Mesopentane.
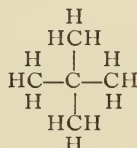
Two Strictly Isomeric Compounds.
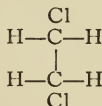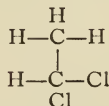
Ethylene chloride.   Ethidene chloride.

II. Two or more compounds are *metameric* when they possess the same elementary substances united with the same percentage composition and the same molecular weight but contain different evident compound radicles. Metamerism is exemplified chiefly, as might be theoretically expected, in ethers, amines, and esters.

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* Cayley, " On the analytical forms called trees, with applications, the theory of chemical combinations." Brit. Assoc. Rep. 1875, 257. Recalculated by Dr. Hermann, of Wurtzburg. (Referred to in Roscoe & Schorlemmer's Chemistry, vol. iii. Part I. p. 122.)

Three Metameric Compounds.

$$N \begin{cases} C_3H_7 \\ H \\ H \end{cases} \qquad N \begin{cases} CH_3 \\ C_2H_5 \\ H \end{cases} \qquad N \begin{cases} CH_3 \\ CH_3 \\ CH_3 \end{cases}$$

Propylamine.   Methylethylamine.   Trimethylamine.
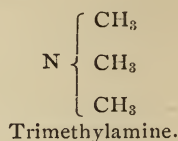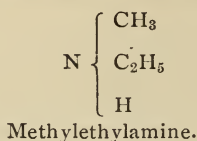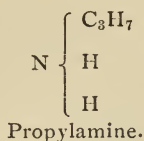
III. Two or more compounds are *polymeric* when they are composed of the same elementary substances with the same percentage composition, but have different molecular weights and different number of atoms in the molecule, and of course different formulas.

Four Polymeric Compounds.

Ethylene, C_2H_4
Propylene, C_3H_6
Butylene, C_4H_8
Amylene, C_5H_{10}
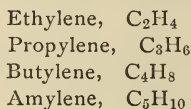
IV. A fourth kind of isomerism, called *physical isomerism, geometrical isomerism, or optical isomerism*, has of late come to be widely accepted. It is a feature of what is called stereo-chemistry; a branch developed through the studies of Le Bel, Van't Hoff and Wislicenus, and others. In this view two adjacent carbon atoms are viewed as having their points of attraction distributed in space as if at the four apexes of a tetrahedron.

When such a carbon atom has its four points of attraction satisfied by *four different atoms or radicles*, it is called an *asymmetric carbon atom*. Evidently another carbon atom may have the same four radicles arranged in a different order. The difference between the two arrangements is such as may appear from inspecting, at the same time, a given tetrahedron and its image reflected from a mirror. A compound may have more than one asymmetric carbon atom.

Lactic acid, $C_3H_6O_3$ or $H_3C \cdot CHOH \cdot COOH$, has one asymmetric carbon atom.

It has been shown that compounds containing one or more asymmetric carbon atoms have — when liquified or in solution — certain influence on the ray of light passing through them.

On the other hand, substances possessing such optical properties are usually assumed to have asymmetric carbon.

V. The isomerism characteristic of *aromatic compounds* is discussed later.

Empirical and Rational Formulas.

In an empirical formula, the atoms are arranged in some order adopted, *but all atoms of a kind are put together.* Thus, the empirical formula of trimethylamine is NC_3H_9.

In a rational formula, however, the atoms are arranged in an order fixed upon after a very careful study of the compound. The rational formula of trimethylamine is $N(CH_3)_3$.

The empirical formula of ethyl alcohol is C_2H_6O. The rational formula of ethyl alcohol is C_2H_5OH.

Saturated and Unsaturated Compounds.

In certain carbon compounds each of the four points of every carbon atom is attached to some chemical element; compounds of this kind are called *saturated;* ethane is an example, C_2H_6.

In other cases, where there exists double or treble linkage between two adjacent carbon atoms the compound is called *unsaturated;* acetylene, C_2H_2, is an example.

It should be noted, however, that double or treble linkage does not imply *greater* molecular stability — quite the contrary, it implies *less.* In a complex compound of this kind when powerful chemical agents are applied, the subdivision of the molecule is most likely to occur at the point where double or treble linkage exists. This view is also sustained by certain experiments of R. Schiff. These have shown that in case of *doubly linked* carbon atoms the atomic volume of the carbon is slightly greater than in *singly linked* carbon atoms.

Molecular Structure of Compounds.

Within the last few years, great progress has been made in the acquisition of knowledge with respect to the *molecular structure* of *certain* organic compounds; yet in the vast majority of cases this molecular structure is yet unknown.

The inorganic compounds have been arranged in a certain order in accordance with their natural affiliations, and though when such arrangement is made some gaps appear, these gaps are of great service in that they suggest that many more compounds than those yet recognized or described may be hereafter produced.

To the organic compounds the same statement may be applied. Gaps in their list point out avenues for future discovery in organic chemistry.

In studying any chemical compound the investigator desires to learn :

First, its qualitative composition.

Second, its quantitative composition. (This includes the percentage amounts of the components, or more, the number of atoms in a molecule.)

Third, the inner atomic grouping or arrangement.

The determination of the qualitative or quantitative composition is not very difficult in cases of most compounds whether inorganic or organic.

But it is often very difficult — in some cases it is, at present, impossible — to determine the *atomic grouping*, or even the *molecular weight* of a compound. In case of many inorganic substances the molecular weight now accepted may be materially changed hereafter.

One of the best guides in the determination of the molecular weight of a substance is its vapor density. Now a larger proportion of organic compounds than of inorganic compounds may be changed to vapor without decomposition. Hence, the true molecular weight is known in more cases in organic chemistry than in inorganic chemistry. But there are some organic substances, as sugar for example, which cannot be changed to vapor without decomposition. Thus their molecular weight cannot be determined by the method stated.

In some cases the molecular formula may be determined by other means.

The determination of the inner atomic grouping of substances has been carried on with what may be considered a high degree of success in case of many of the carbon compounds; but the methods employed are so various as to make it impracticable to undertake a discussion of them here.

The fact that carbon forms so large a nnmber of compounds, many of which differ one from another by the addition of easily transferred radicles, makes comparisons of chemical and physical properties easier than in the case of the atoms of inorganic chemistry. Thus organic chemistry seems to be likely to throw great light upon the field of inorganic chemistry.

Organic Compounds Classified.

The difficulty of classifying organic compounds is of course very great. This is due, *first*, to their great number; *second*, to the many relationships of one and the same substance; *third*, to the relative imperfection of our acquaintance with the most of them.

Those organic substances with which chemists are best acquainted are arranged for discussion in many different ways. But they are almost always arranged in four great groups :

1st. Fatty compounds. This group includes most of the open-chain compounds. They are usually considered as derivatives of marsh gas, CH_4. (They are not necessarily oily or greasy — they may be quite otherwise.)

2d. Aromatic compounds. These are closed chain compounds. Many of them contain one or more benzene nuclei, $(C_6.)$

3d. Other less easily classified vegetable matters.

4th. Other less easily classified animal matters.

Carbon and Silicon Compared.

The silicon atom, like the carbon atom, has four points of attraction. Silicon also forms certain compounds, closely analogous to well known organic compounds, the difference consisting merely in a replacement of carbon by silicon. Undoubtedly, silicon forms a vast number of compounds — witness the great variety of silicious rocks known. Indeed silicon is the characteristic element of the mineral kingdom as carbon is of the organic kingdoms. But chemists know less of the structure of silicon compounds because these cannot be easily dissolved or volatilized or decomposed as carbon compounds can.

CHAPTER II.

THE STUDY OF ORGANIC COMPOUNDS.

Ultimate Analysis and Proximate Analysis.

In the study of a given organic compound, there may be at least three different kinds of work to be conducted. *First,* the substance itself should be produced or prepared in a pure condition, *i. e.,* free from admixture with any other substance. *Second,* the qualitative and quantitative composition should be learned ; it is comparatively easy to determine the percentage proportions of the different elements making up the molecule. *Third,* the arrangement of atoms in the molecule should be learned ; this is often a very difficult task. To secure the knowledge desired, a vast amount of chemical work must be done, and the results of such work must be carefully compared and finally employed in a logical way.

Most organic compounds contain two or more of the following elements : carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus. Many artificial organic compounds may contain in addition to two or more of those already mentioned, one or more of the halogens, chlorine, bromine, iodine. Further, many organic compounds may contain one or more of the non-metals, or even of the metals.

The analysis of organic compounds is of two kinds : ultimate analysis and proximate analysis.

In ultimate analysis, the several elementary constituents of an organic substance are detected, and their amounts determined.

In proximate analysis, one or several radicles, present in the compound, are isolated. (In another kind of proximate analysis, one or more distinct chemical compounds, existing in a mixture, may be separated as individuals and their amounts determined.)

Ultimate Analysis.

The ultimate analysis of an organic compound may involve several sets of processes.

First Process, the determination of carbon and hydrogen. This is usually conducted by a single operation.

Second Process, the determination of nitrogen.

Third Process, the determination of sulphur.

Fourth Process, the determination of phosphorus.

Fifth Process, the determination of chlorine or other halogen.

Sixth Process or Processes, the determination or determinations of other non-metals or metals.

Oxygen is usually determined by difference; that is, by subtracting the sum of the other components from the total.

The Determination of Carbon and Hydrogen. This is usually accomplished by oxidizing the elements mentioned, into carbon dioxide, CO_2, and water, H_2O, respectively.

The operation is usually conducted in a special apparatus. The apparatus consists essentially of four parts: *First*, a combustion furnace. It is composed of a set of supports; these are for the tube (usually of glass, sometimes of porcelain,) in which the substance to be tested is burned. It has also a set of gas burners capable of heating the combustion tube and its contents. *Second*, the combustion tube. It is intended to contain a mixture of the substance to be tested and some oxidizing agent (such as cupric oxide, CuO, or lead chromate, $PbCrO_4$,) which easily furnishes oxygen to the organic substance under examination. Sometimes a small quantity of potassium chlorate (which is easily made to liberate oxygen) is placed at the rear end of the tube. *Third*, the rear end of the tube is often supplied with a current of oxygen gas from a gas holder. Of course the gas must pass through purifiers before use, that is, it must be freed from carbon dioxide and moisture before it is used. *Fourth*, the absorption apparatus. At its forward end the combustion tube connects with a set of bulbs, one or more to absorb the water, and one or more to absorb the carbon dioxide, produced by the combustion. These tubes are usually weighed before and after a given test. Any gain in weight of the one set is due to water absorbed and this is referable to hydrogen of the original organic substance. Likewise any gain in weight of the other set is due to carbon dioxide absorbed, and this is referable to the carbon of the organic substance.

Determination of Nitrogen. Absolute Method. This method depends upon such a combustion of the organic matter as will separate nitrogen in the gaseous form, any other substances produced being retained by suitable absorption tubes. The nitrogen is then carried on to a glass measuring tube. From the amount of nitrogen gas obtained in the measuring tube, the amount in the organic substance under investigation is determined.

Determination of Nitrogen. Soda-Lime Method. By this method, the organic matter is heated in a combustion tube in contact with a peculiar mixture of sodium hydroxide and calcium oxide, called soda-lime. This powerful alkaline material withdraws carbon and oxygen from the organic matter to form sodium carbonate or calcium carbonate, or both. At the same time the nitrogen and hydrogen of the organic substance form ammonia gas, NH_3. This gas is carried forward to a suitable absorption apparatus, containing sulphuric acid

or hydrochloric acid, by which it is retained. Subsequently, the amount of ammonia is learned by usual methods of analysis. Thence, the amount of nitrogen in the original compound may be computed.   .

Determination of Nitrogen.   Wanklyn Method.   This method depends upon the fact that when nitrogenous organic substances are boiled in an alkaline solution of potassium per-manganate, this salt accomplishes a special kind of oxidation.   It leaves, however, the nitrogen and the hydrogen in a form such that they combine to produce ammonia gas.   In Wanklyn's method this ammonia gas is distilled from the liquid containing it and caught in a receiver.   The amount of ammonia in the receiver is determined by the depth of color it produces in the Nessler solution.

Determination of Nitrogen.   The Kjeldahl Method.   In this process the organic matter is decomposed by sulphuric acid in presence of powdered zinc under the influence of heat.   The zinc liberates hydrogen in such a form that it combines with the nitrogen to form ammonia gas.   The latter substance, however, immediately unites with the sulphuric acid to form ammonium sulphate. The liquid mass is subsequently distilled with sodium hydroxide.   The ammonia being expelled and steam being driven off, the two condense together as a clear liquid.   In this liquid, ammonia may be determined volumetrically by a solution of standard acid.

Determination of Sulphur.   One method is to fuse the material with potassium hydroxide and potassium nitrate.   The sulphur is oxidized into a sulphate, which may be subsequently detected and determined by the use of barium chloride.

Another method (suitable for detection rather than determination) is to fuse the organic compound with potassium hydroxide alone : potassium sulphide results.   By placing the solid mass upon a clean silver coin, the silver becomes darkened from the formation of silver sulphide.

Another method is to fuse the organic compound with potassium carbonate. A potassium sulphide is formed which is capable of giving a purple coloration with sodium nitro-prussiate.

Determination of Phosphorus.   The ordinary method is to fuse the material with potassium hydroxide and potassium nitrate.   The process is oxidizing; the phosphorus being turned into a phosphate.   This is subsequently detected and determined by the ammonium molybdate or other well-known methods.

Determination of Chlorine and other halogens.   For this purpose many processes may be employed, the general effort being to separate the chlorine or other halogens from the original compound and get it into the form of a soluble chloride, bromide, etc.   In this soluble salt the halogen is detected and may be estimated by means of some silver salt.

Determination of other Elements, Metals, etc.   In this case the organic substance is heated either alone or with some suitable chemical agents, the more volatile constituents being expelled.   Then the metals may be left as carbonates which are capable of subsequent analysis by ordinary methods.

Proximate Analysis.

Speaking generally, proximate analysis has for its purpose the separation of *certain compounds which exist in a mixture* of sub-

stances. Thus the proximate analysis of wheat flour may have for its purpose the determination of the several amounts of starch, protein, crude fibre, fat, and perhaps other materials existing in the flour. Analyses of this kind may be considered as separations of compounds mechanically associated.

But further, the term proximate analysis may be applied to the detection of the *various radicles existing in a complex organic molecule*. Incidentally it may be necessary in case of fatty compounds, and yet more in case of aromatic compounds, to determine the position certain radicles hold in the molecules.

As a very simple example, a substance having the ultimate composition CH_3NO_2 may be mentioned. This formula represents two very different compounds; the one is nitro methane, CH_3-NO_2, the other is methyl nitrite CH_3-O-NO. It may be necessary to prove the presence of the methyl radicle; it may further be necessary to determine whether the *nitrogen* is *directly* combined with the methyl or whether it is linked to the methyl by an atom of oxygen.

In the case in question the work is comparatively simple. Under the influence of reducing agents such as nascent hydrogen, the nitro compounds yield almost invariably *amines*, compounds containing the group NH_2 in which the nitrogen is directly united to the alkyl radicle.

On the other hand nitrogen esters easily yield *alcohol*.

If, therefore, under the action of reducing agents upon the substances in question, methylamine remains, it is evident that the original substance was nitro methane. On the other hand if methyl alcohol is easily produced, it is evident that the original substance was methyl nitrite.

In order to distinguish, then, the inner atomic grouping of a complex organic molecule, certain general methods have been devised similar to those just described.

The processes of proximate analysis are too numerous and varied to admit of compact statement here. Some of them are incidentally presented in succeeding chapters.

CHAPTER III.

PROXIMATE METAMORPHOSIS OF ORGANIC BODIES.

The Subject Considered, Primarily, with Respect to the Operations Performed.

In the preparation of a given organic compound, two general courses naturally suggest themselves. The one course is to construct the desired compound from the elements. Such building up of the organic molecule is often called organic synthesis. Very few organic substances can be produced in this way by the chemist. Any chemist who shows how to build up a new organic molecule synthetically from its chemical elements has secured a distinct triumph. In a certain sense, organic compounds found in nature may be said to be formed by synthesis (upon close examination, however, this statement must be accepted with some limitations).

In many cases an organic compound is obtained by the chemist by mere processes of purification, or separation from a mixture containing it, found in animal or vegetable substances. The preparation of cane sugar from the sugar cane or from the sugar beet, is an example.

In a great many cases, an organic compound is produced by chemical operations performed upon some other compound found in nature. Sometimes the operation represents the production of a less complex artificial organic compound from a more complex natural compound.

General List of Methods.

An organic compound may be formed :

(a) By a direct combination of elements — organic synthesis ;

(b) By the addition of an element or a radicle to a compound already formed ;

(14)

(c) By the substitution of one or more elements or radicles in the place of suitable constituents of a given organic compound;

(d) By the withdrawal of one or more elements or radicles, by the influence of some chemical agent having affinity for them;

(e) By processes analogous to fermentation, digestion, and the like, carried on under the influence of living beings — of the higher animals or plants on the one hand, or of microbes on the other;

(f) By the influence of certain forms of energy, like that of heat in processes of fractional or of destructive distillation; or like that of electricity in the processes of electrolysis.

Special Results Sought.

Among the chief *operations* to be performed, the following should be kept clearly in mind.   The chemist may need:

(a) To add or to subtract oxygen from a compound;

(b) To add or to subtract hydrogen from a compound;

(c) To add or to subtract a halogen from a compound;

(d) To add or to subtract hydroxyl, HO, from a compound;

(e) To add or to subtract combined water (as distinguished from hygroscopic water) from a compound;

(f) To unite, by replacement or otherwise, an acid radicle with a compound, or to withdraw such a radicle;

(g) To secure the ordinary action of an alkali upon a compound, or to withdraw an alkali metal;

(h) To provide for promptly taking up subordinate products of an operation, so that such products may not interfere later;

(i) To perform certain special operations, not easily classified or described, except in large detail.

1.   Oxygen may be added to organic compounds by the mere action of atmospheric air at ordinary temperature or at high temperature, or by means of ozone, or by oxidizing compounds like hydrogen dioxide, nitric acid, or peroxide of lead, or by oxidizing mixtures like

Caustic alkalies and moist silver oxide,

Sulphuric acid and potassium dichromate,

Sulphuric acid and manganese dioxide,

Hydrochloric, sulphuric, or nitric acid, either of these with potassium chlorate.

Potassium hydroxide or sodium hydroxide, as solids, when fused with certain organic compounds, have an oxidizing action. A somewhat similar action is illustrated below (but without fusion):

$$C_2H_5OH \quad + \quad KOH \quad = \quad KOOC.CH_3 \quad + \quad 2H_2$$

| Ethyl alcohol, | Potassium hydroxide, | Potassium acetate, | Water. |

Chlorine and the other halogens in presence of water tend to withdraw hydrogen, liberating oxygen — thus their action becomes oxidizing.

2.   Oxygen may be withdrawn from organic compounds by reducing agents.   Nascent hydrogen exercises reducing action, drawing from organic compounds their oxygen or chlorine or other electro-negative elements.   Thus, nascent hydrogen may reduce nitro-substitution compounds to amines ; for example, nitrobenzene to phenylamine, called aniline, as follows :

$$(C_6H_5)NO_2 + 3H_2 = (C_6H_5)NH_2 + 2H_2O$$
Nitrobenzene   Aniline
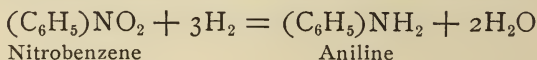
The hydrogen may be generated by the use of zinc and sulphuric acid, or by zinc and sodium hydroxide, or by iron filings with acetic acid, or by other methods.

Metallic elements even have similar effect.   Thus, powdered zinc is reducing.   Again, sodium amalgam is reducing.

3.   Hydrogen may be added to organic compounds or introduced into them.

Thus, aldehyde with sodium amalgam and water produces ethyl alcohol.

Production of Hydrogen :

$$2H_2O + 2NaHg = H_2 + 2NaOH + 2Hg$$

Production of Ethyl Alcohol from Aldehyde :

$$C_2H_4O + H_2 = C_2H_5OH$$
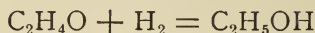
4.   Hydrogen may be withdrawn from organic compounds.

Thus, methyl alcohol and metallic potassium yield free hydrogen :

$$2CH_3OH + K_2 = 2CH_3OK + H_2$$
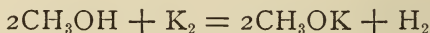
5.   Chlorine and the other halogens may be added to organic compounds.   The following are examples :

C_2H_4	$+$	Cl_2	$=$	$C_2H_4Cl_2$
Ethylene		Chlorine		Ethylene chloride
C_6H_6	$+$	$3Cl_2$	$=$	$C_6H_6Cl_6$
Benzene		Chlorine		Benzene hexachloride
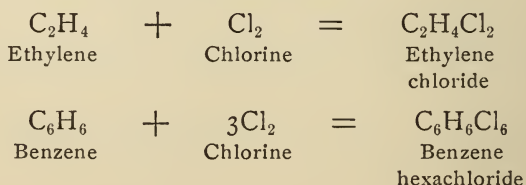
Phosphorus pentachloride, PCl_5, and phosphorus pentabromide, PBr_5, are so unstable that they easily part with a portion of the halogen present — the latter then acts much as it does in the free condition.

$$C_2H_4O \quad + \quad PCl_5 \quad = \quad C_2H_4Cl_2 \quad + \quad POCl_2$$

Aldehyde	Phosphorus pentachloride	Ethylene chloride	Phosphorus oxychloride

In some cases the halogens act substitutingly : they replace hydrogen.

6. Chlorine and the other halogens may be withdrawn from organic compounds. Thus, ethyl iodide gives up its iodine to powdered zinc :

$$2C_2H_5I \quad + \quad Zn \quad = \quad ZnI_2 \quad + \quad C_4H_{10}$$

Ethyl iodide	Zinc	Zinc iodide	Butane
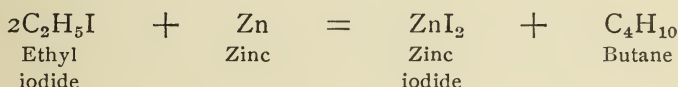
7. The hydroxyl group, HO, may be withdrawn from organic compounds.

Phosphorus trichloride, PCl_3, phosphorus tribromide, PBr_3, phosphorus oxychloride, $POCl_3$, tend to remove the hydroxyl group, HO, and at the same time replace it by the halogen present.

$$3C_2H_5OH \quad + \quad PCl_3 \quad = \quad 3C_2H_5Cl \quad + \quad H_3PO_3$$

Ethyl alcohol	Phosphorus trichloride	Ethyl chloride	Phosphorus acid
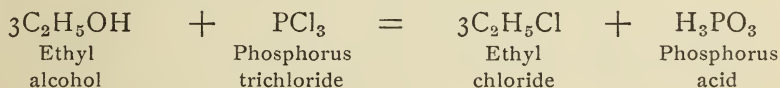
Hydrochloric acid or hydrobromic acid may have a similar kind of action :

$$C_2H_5OH \quad + \quad HCl \quad = \quad C_2H_5Cl \quad + \quad H_2O$$

Ethyl alcohol	Hydrochloric acid	Ethyl chloride	Water
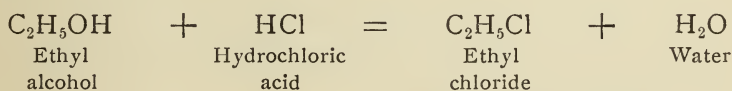
8. The hydroxyl group, HO, may be added to organic compounds.

Thus, methyl bromide and sodium hydroxide react :

$$CH_3Br + NaOH = CH_3OH + NaBr$$
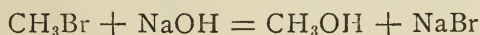
9. One or more molecules of water may be added to organic compounds.

2

Dilute sulphuric acid occasionally leads to such addition of water. Thus, cane sugar, upon long boiling with dilute sulphuric acid, forms glucose.

$$C_{12}H_{22}O_{11} + H_2O + H_2SO_4 \cdot Aq = 2(C_6H_{12}O_6) + H_2SO_4 \cdot Aq*$$
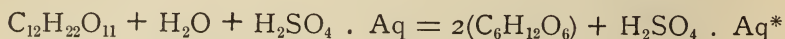
10.   One or more molecules of water, H_2O, may be withdrawn from organic compounds containing hydrogen and oxygen, even when they do not exist as water in the compound.

Concentrated sulphuric acid withdraws the constituents of water from ethyl alcohol, forming ethylene.

$$C_2H_5OH + H_2SO_4 = C_2H_4 + H_2O + H_2SO_4$$
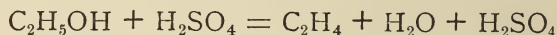
11.   An acid radicle may be added to an organic radicle.

Thus, nitric acid may form an ester — an ethereal salt :

$$C_2H_5OH \quad + \quad HNO_3 \quad = \quad C_2H_5NO_3 \quad + \quad HOH$$

Ethyl   Nitric   Ethyl   Water
alcohol   acid   nitrate
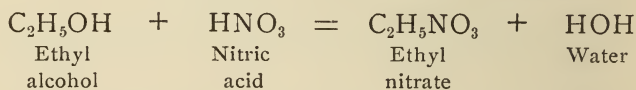
Again, methyl alcohol, distilled with strong sulphuric acid, produces methyl sulphate, an ester, as follows :

$$2(CH_3OH) + H_2SO_4 = (CH_3)_2SO_4 + 2H_2O$$
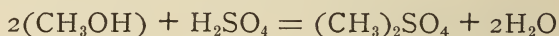
12.   An acid radicle may be withdrawn from an organic molecule.

Thus, ethyl sulphate upon addition of potassium hydroxide, parts with the acid radicle :

$$(C_2H_5)_2SO_4 + 2KOH = K_2SO_4 + 2C_2H_5OH$$
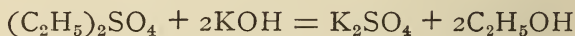
13.   Subordinate products may be gotten out of the way of the chief products of a reaction.

Thus in some cases where iodine is used it forms hydriodic acid, which would interfere with a desired reaction. Then the presence of nitric acid or iodic acid or some similar agent may remove the hydriodic acid.

$$5HI + HIO_3 = 3I_2 + 3H_2O$$

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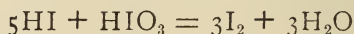
* Aq. signifies an imperfectly defined quantity of water.

14. Certain other special operations may be noted here :

By the addition of a great variety of reagents, compound radicles may be transferred from an organic substance to some other substance. Thus, methyl chloride, CH_3Cl, distilled with potassium hydroxide, KOH, has its methyl transferred away from the original molecule, as follows :

$$CH_3Cl + KOH = CH_3OH + KCl$$
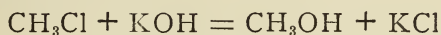
15. Observe also that the oxidizing action of nitric acid may be attended with an action of substitution.

Thus, nitric acid acts on benzene to produce nitrobenzene, as follows :

$$C_6H_6 \quad + \quad HNO_3 \quad = \quad C_6H_5NO_2 \quad + \quad H_2O$$

| Benzene | Nitric acid | Nitro-benzene | Water |
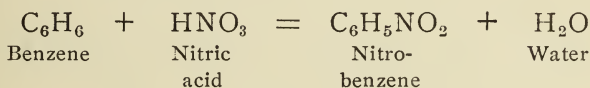
16. Sulphuric acid performs the operation called sulphonation — adding the group HSO_3 — for example :

$$C_6H_6 \quad + \quad H_2SO_4 \quad = \quad C_6H_5HSO_3 \quad + \quad H_2O$$

| Benzene | Sulphuric acid | Benzosulphonic acid | Water |
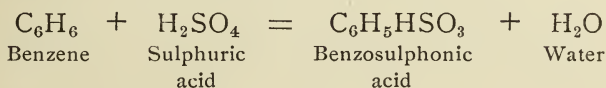
Heat may lead to the union of certain substances to produce organic compounds. For example, cyanogen gas in a suitable receiver, may be passed over potassium under such conditions that when the potassium is heated, chemical union may take place with the formation of potassium cyanide. Again, an electric current of some sort may lead elements to combine. In this way, carbon electrodes introduced into a jar containing hydrogen may be led under the influence of the electric current, to produce acetylene by the union of carbon and hydrogen.

Heat is an agent which is very much used in artificial metamorphoses of organic compounds, as well as in other chemical operations. In chemical operations generally, heat gives rise, according to circumstances, to the combination of chemical substances or to their decomposition. So among organic compounds in certain cases, heat gives rise (1) to a union of somewhat simple molecules to produce more complex ones; (2) to a union such as develops several new molecules from one complex one with simultaneous addition of constituents; (3) to a splitting up of complex molecules into those less complex. This third kind of operation is of great importance in organic chemistry. The kind of decomposition which a given organic molecule undergoes, varies very much with the conditions of the heating. A moderate addition of heat may

produce one kind of change, while a much more considerable addition, favored, may be, by pressure (as when the organic matter is heated in a closed iron tube or digester), may produce a very different sort of decomposition. This sort of action may be looked upon as a form of dissociation. Many excellent examples of it are of great practical importance. Thus, in what is called the *destructive distillation* of coal in the manufacture of illuminating gas, the molecules composing the coal are decomposed into a vast number of new molecules, the *gas* derived from the coal containing for example, marsh gas, CH_4, and ethylene, C_2H_4. The *tarry liquids* contain molecules of benzene, C_6H_6, anthracene, $C_{14}H_{10}$, and other important ones. Again, the destructive distillation of wood produces a decomposition of the molecules of the wood, giving rise to the formation of molecules of acetic acid, $HOOC \cdot CH_3$, methyl alcohol, CH_3OH, as well as many others. The action of heat in what is called *fractional distillation* must not be confounded with the action just described.

Fractional Distillation. The process of fractional distillation is much used in organic chemistry. When a mixture of two substances having different boiling points, is placed in a retort and heated moderately, it is found that the boiling point of the mixture rises by more or less distinct steps. A series of different distillates is produced. If the distillates are received in separate bottles, according with each changing step of boiling point, the bottles may be found to contain distinctly separate substances. Thus, a mixture of ethyl alcohol and water distilled in a flask, gives different distillates. The earlier distillates are richer in alcohol. The later distillates are nearly pure water.

This process of fractional distillation is much used in the arts as well as in organic chemistry.

In the treatment of crude petroleum, fractional distillation is skilfully used. A given petroleum as it flows from the earth, is a mixture of a very large number of hydrocarbons. By skilful and repeated fractional distillations these may be separated one from another so that each one of the several selected distillates may be found to be a practically homogeneous compound.

To recapitulate under the head of *agents* (either reagents or forces) rather than under the head of operations :

1. Oxygen is oxidizing. The oxygen may be added or it may oxidize hydrogen and expel it as water.

2. Ozone acts like oxygen only more energetically.

3. Hydrogen peroxide, H_2O_2, acts like ozone.

4. Hydrogen, especially in the nascent state, is reducing. It withdraws oxygen and the halogens.

5. Powdered zinc acts like hydrogen. (In certain cases the zinc itself enters the molecule.)

6. The alkali metals, or their amalgams, act like zinc. (In certain cases these metals enter the molecule.)

7. The halogens enter in a substituting way (taking the place of hydrogen). Or they add themselves to the molecule.

8. Phosphorus trichloride, also bromide, and phosphorus oxy-chloride, $POCl_3$, may remove the hydroxyl group, HO, and they may replace it by the halogen present.

9. Phosphorus pentachloride, also bromide, may set free a part of the halogen to act directly.

10. Hydrochloric acid may act simply as an acid to combine with suitable radicles.

11. Nitric acid may act simply as an acid to combine with suitable radicles.

Or it may act as an oxidizing agent.

Or it may act substitutingly, forming nitro-compounds.

Or it may destroy subordinate interfering products.

12. Sulphuric acid may act simply as an acid to combine with suitable radicles.

Or it may withdraw water from compounds containing hydrogen and oxygen.

Or it may sulphonate compounds, substituting the group HSO_3.

13. Sodium hydroxide or potassium hydroxide may act simply as alkalies.

Or they may, when fused dry, have an oxidizing action.

Or in case of nitrogen compounds they may withdraw the elements C and O (to form alkaline carbonates) thus liberating ammonia gas.

14. Potassium permanganate,
    Potassium dichromate,
    Cupric oxide, may act as oxidizing agents.

15. Ferments of a specific character may produce specific compounds.

16. Heat acts dissociatively.

17. Electricity may stimulate union of elements; oftener it may act dissociatively.

CHAPTER IV.

PROXIMATE METAMORPHOSIS OF ORGANIC COMPOUNDS.

The Subject Considered with Reference to the Products Obtained.

It has already been stated as a fundamental principle of organic chemistry, that certain organic radicles act in a general way like elements. Just as different metals form halogen compounds, oxygen compounds, hydroxides, sulphates, nitrates, etc., so do the *electro-positive* organic radicles. It should be noted that in inorganic chemistry certain elements are called *electro-negative* (although this classification is based upon *relative* characteristics rather than upon absolute). So, in organic chemistry, certain radicles, generally oxyhydrocarbons, act like non-metals. Thus, as the non-metals of inorganic chemistry tend to form acid anhydrides and then acids and then enter into the formation of salts (in this case, by union with electro-positive elements or compounds); so those organic radicles which correspond to non-metals, may form salts with those organic radicles that correspond to metals. These analogies may be easier comprehended by study of the following table :

Methyl,	CH_3	Acetyl,	$- OC \cdot CH_3$
Methyl hydride,	CH_3H	Acetic aldehyde,	$HOC \cdot CH_3$
Methyl chloride,	CH_3Cl	Acetyl chloride,	$ClOC:CH_3$
Methyl ether,	$(CH_3)_2O$		
Methylethyl ether,	$CH_3C_2H_5O$		
Methyl alcohol,	CH_3OH	Acetic acid,	$HOOC \cdot CH_3$

$$\text{Methyl — acetate}$$
$$Cr_3 — O — OC \cdot CH_3$$

$$K_2O \ + \ 2(HONO_2) \ = \ 2KONO_2 \ + \ H_2O$$

Potassium oxide   Nitric acid   Potassium nitrate

$$(CH_3)_2O \ + \ 2(HOOC \cdot CH_3) \ = \ 2(CH_3OOC \cdot CH_3) \ + \ H_2O$$

Methyl oxide   Acetic acid   Methyl acetate
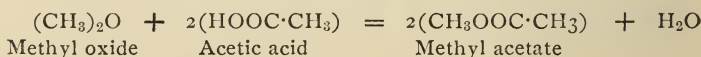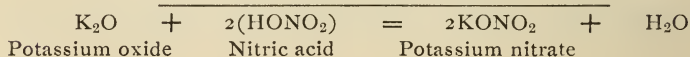
Certain forms of transformation of one organic compound into another, are stated below. It may be noted, *first,* that only the easier understood transformations are represented; and *second,* that, as far as possible, only two sets of radicles are employed in the examples (the first set commencing with ethyl, the second set commencing with acetyl.)

(1) The *hydrocarbon radicles* are viewed as the starting points. Thus, the hydrocarbon radicle ethyl, C_2H_5, the equivalent of a metal, is capable of nearly all the transformations mentioned below. *These radicles are often called alkyl radicles.*

(2) *Hydrides* are formed by the mere union of hydrogen with hydrocarbon radicles. Thus, ethyl forms ethyl hydride, C_2H_5H, called ethane.

(3) *Halogen compounds* are formed by direct union of halogen elements (chlorine, bromine, iodine, fluorine,) with the organic radicles. Thus, ethyl forms ethyl chloride, C_2H_5Cl.

(4) *Oxides, called ethers,* are formed after the water type. Thus, ethyl forms the oxide $(C_2H_5)_2O$, called ethyl ether. Ethers are called simple when but one kind of radicle is present. If more than one kind of radicle is present, they are called mixed. Thus, methyl and ethyl may form together an oxide which is called a mixed ether, $CH_3C_2H_5O$, methylethyl ether.

(5) *Hydroxides,* called alcohols, are formed also after the water type. In forming alcohols, only one-half of the hydrogen of water is replaced by the organic radicle. Thus, ethyl alcohol is C_2H_5OH.

The ordinary alcohols are of three kinds, called primary, secondary, and tertiary. The classification is based on the structure of the alcohol; their recognition is experimentally based on the products derived from their subsequent oxidation.

(6) *Organic acids.* Any given organic acid contains one or more molecules of carboxyl, HOOC—. Thus acetic acid is $HOOC \cdot CH_3$.

The hydrogen atom of the carboxyl is replaceable by metal so as to form a salt.

Thus acetic acid forms potassium acetate, $KOOC \cdot CH_3$.

The following partial list is worthy of note :

Formic acid,	$HOOC \cdot H$	Potassium formate,	$KOOC \cdot H$
Acetic acid,	$HOOC \cdot CH_3$	Potassium acetate,	$KOOC \cdot CH_3$
Propionic acid,	$HOOC \cdot C_2H_5$	Potassium propionate,	$KOOC \cdot C_2H_5$
Butyric acid,	$HOOC \cdot C_3H_7$	Potassium butyrate,	$KOOC \cdot C_3H_7$
		etc.	

They also form organic salts which are known as *esters*. A simple example is found in ethyl acetic ester, ethyl acetate, $(C_2H_5)OOC \cdot CH_3$.

(7)   *Aldehydes*, are characterized by one molecule of carboxyl, CO, acting as an intermediate link of connection between the hydrogen on the one hand and a hydrocarbon radicle on the other :

$$\text{Acetic aldehyde,}\quad C_2H_4O = CH_3(CO)H$$

$$
\begin{array}{c}
\text{H} \\
\text{HC—C—H} \\
\text{H O}
\end{array}
$$
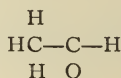
(8)   *Ketones*, have an oxide of carbon, carbonyl, CO, acting as an intermediate link of connection between two radicles. (The radicles may be alike or different.)   Thus, the ordinary ketone known as acetone, or methyl ketone, is CH_3COCH_3.

$$
\text{Methyl ketone (acetone),}\quad CH_3 \cdot CO \cdot CH_3,\quad
\begin{array}{cc}
\text{H} & \text{H} \\
\text{HC—C—CH} \\
\text{H O H}
\end{array}
$$
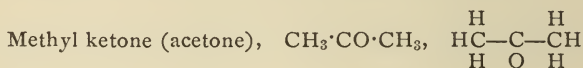
(9)   *Triad nitrogen (phosphorus, arsenic, antimony,) compounds.* These are called amines (phosphines, arsines, stibines,) amides, imides, amic acids, ureas (and others.)

The inorganic types are ammonia gas, NH_3, phosphine, PH_3, arsine, As H_3, stibine, Sb H_3.

Examples: Menthylamine, $NH_2 CH_3$,

$$
\begin{array}{c}
\text{H} \\
\text{H H HCH} \\
|\quad |\quad | \\
\underbrace{\qquad\qquad} \\
\text{N}
\end{array}
$$

Formamide, $NH_2 \cdot COH$,

$$
\begin{array}{c}
\text{H} \\
\text{H H CO} \\
|\quad |\quad | \\
\underbrace{\qquad\qquad} \\
\text{N}
\end{array}
$$

Carbimide, NH·CO,

$$\begin{array}{c} \quad\ O \\ H \quad -C- \\ |\qquad| \\ \underbrace{\qquad\qquad} \\ N \end{array}$$

Carbamic acid, $NH_2 \cdot COOH$,

$$\begin{array}{c} \qquad\qquad H \\ \qquad\qquad | \\ \qquad\quad O\ O \\ \qquad\quad |\,|\,| \\ H\ \ H\ \ C \\ |\quad|\quad \\ \underbrace{\qquad\qquad} \\ N \end{array}$$

Urea, $NH_2 \cdot CO \cdot NH_2$,

$$\begin{array}{c} H\ \ H\quad O\quad H\ \ H \\ |\quad|\quad C\quad|\quad| \\ \underbrace{\quad\ }\ \ \underbrace{\quad\ } \\ N\qquad\quad N \end{array}$$

Sulphourea, $NH_2 \cdot CS \cdot NH_2$,

$$\begin{array}{c} H\ \ H\quad S\quad H\ \ H \\ |\quad|\quad C\quad|\quad| \\ \underbrace{\quad\ }\ \ \underbrace{\quad\ } \\ N\qquad\quad N \end{array}$$

Methylurea, NH $CH_3 \cdot CO \cdot NH_2$,

$$\begin{array}{c} \qquad\quad H \\ H\ HCH\ O\quad H\quad H \\ |\quad|\qquad C\quad|\quad| \\ \underbrace{\quad\ }\ \ \underbrace{\quad\ } \\ N\qquad\quad N \end{array}$$
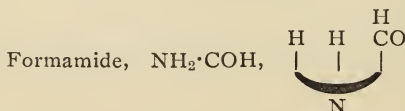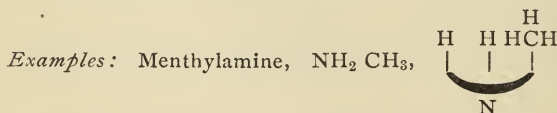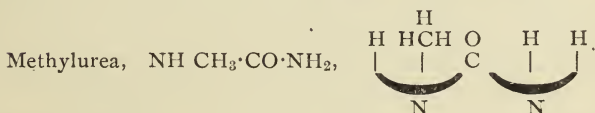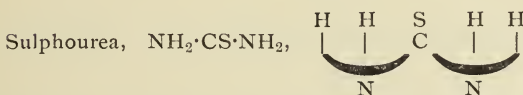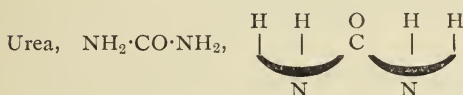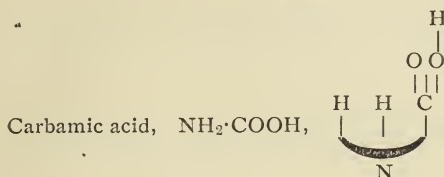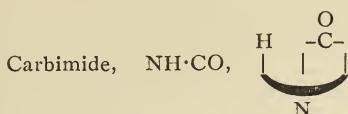
(10) *Pentad nitrogen (phosphorus, arsenic, antimony,) compounds.* These are substituted ammonium (phosphonium, arsonium, stibonium,) salts, such as halides and ternary salts.

The inorganic types are ammonium chloride, NH_4Cl, ammonium nitrate, $NH_4 NO_3$, ammonium sulphate, $(NH_4)_2SO_4$, ammonium phosphate, $(NH_4)_3PO_4$, etc.

Examples: Methylammonium chloride, $NH_3CH_3 \cdot Cl$,

$$\begin{array}{c} \qquad\qquad\quad H \\ H\ \ H\ \ H\ \ HCH\ \ Cl \\ |\quad|\quad|\qquad|\qquad| \\ \underline{\qquad\qquad\qquad\qquad} \\ N \end{array}$$

Methylammonium nitrate, $N Me_4 NO_3$
Ethylammonium sulphate, $(N Et_4)_2 SO_4$
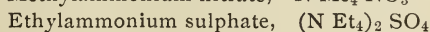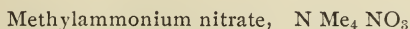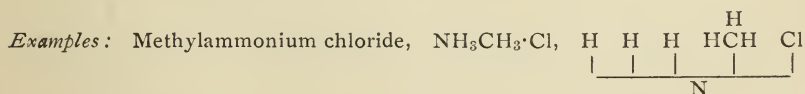
(11) *Sulphonic compounds.* Compounds containing one or more groups of the radicle, HSO_3, *directly united to the hydrocarbon radicle.*

Example: Methyl sulphonic acid, $CH_3 \cdot SO_3H$

$$\begin{array}{c} \qquad\qquad\qquad H \\ \qquad H\qquad\qquad | \\ HCH\ \ O\quad O\ \ O \\ |\quad|\quad|\quad|\quad|\,| \\ \underline{\qquad\qquad\qquad} \\ S \end{array}$$
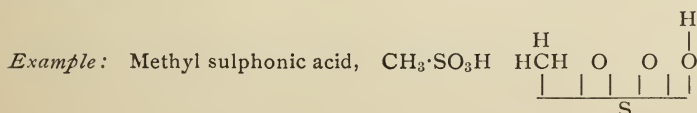
NOTE.—Sulphonic compounds must be carefully distinguished from organic sulphates and sulphites, for example from such salts as methyl sulphate, $(CH_3)_2SO_4$

(12) *Nitro-compounds.*   Compounds containing one or more groups of the radicle NO_2, *directly united with the hydrocarbon radicle.*

$$\text{Example: Nitro-methane, } \underset{H}{\overset{H}{HC}}\!\!-\!\!-\!\!-NO_2$$

NOTE.—Nitro-compounds must be carefully distinguished from organic nitrites and nitrates.

$$\text{Examples: Methyl nitrite (an isomer of nitromethane), } \underset{H}{\overset{H}{HC}}\!\!-\!\!O\!\!-\!\!NO$$

$$\text{Methyl nitrate, } \underset{H}{\overset{H}{HC}}\!\!-\!\!O\!\!-\!\!NO_2$$

(13) *Organo-metallic* bodies are formed by a proper combination of certain metals with compound radicles.   Such compounds may assume a great variety of forms.   In all cases, however, their construction is after the type of examples discussed.   As it has been shown that in mixed ethers and esters, more than one organic radicle may be present, it should not be unexpected that even a metal — the simple radicle of the inorganic chemist — may take the place of an organic radicle, such as has before been called, in certain cases, the metal of the organic chemist.

CHAPTER V.

BINARY CARBON COMPOUNDS.

Compounds Containing Hydrogen, or Chlorine or Oxygen or Sulphur.

I. Compounds of Carbon and Hydrogen.

Carbon combines with hydrogen in a large number of different proportions and by a great many different methods. The two elements mentioned thus form an enormous number of substances included in the important class called the hydrocarbons.

The hydrocarbons are usually divided into two great groups ; the one is called the *fatty* or open chain group, the other is called the *aromatic* or the closed chain group.

Members of the *fatty group* are found in nature in petroleum oils and in what is known as natural gas. Petroleum oils come to the surface through natural crevices or through artificial wells bored for the purpose of securing them. Natural gas is obtained in a similar manner. Petroleum, and natural gas as well, are mixtures of different substances. Certain of the more volatile liquids obtainable from petroleum are known in commerce under the names, naphtha, gasolene, benzine. The last name is an unfortunate one. It sometimes introduces a misapprehension from its close resemblance to the word benzene, the latter applying properly to a hydrocarbon, C_6H_6 of the aromatic series.

The *aromatic hydrocarbons* do not exist in abundance in nature ; they are oftener produced by the decomposition of certain organic substances.

Chemists accept as the primary substance of the fatty series, the compound, CH_4, called marsh gas. By proper chemical operations leading to the addition of elements or radicles, marsh gas may be modified or added to in such a way as to build up much more complex organic compounds of its group.

Chemists generally accept as the primary substance of the aromatic series the compound, C_6H_6, called benzene. This substance is a volatile liquid. It

is usually obtained by the fractional distillation of the coal-tar produced in the manufacture of illuminating gas.

A more extended discussion of the hydrocarbons will be presented later.

II. Compounds of Carbon and Chlorine.

With chlorine, carbon forms the compound carbon tetrachloride, CCl_4. This substance is looked upon as equivalent to marsh gas, CH_4, in which the hydrogen atoms have been replaced by chlorine atoms. The propriety of this view is found in the fact that a series of compounds may be produced, of which the following is a list :

$$CH_4 \qquad CH_3Cl \qquad CH_2Cl_2 \qquad CHCl_3 \qquad CCl_4$$

It is evident that this series represents gradual and progressive replacement of hydrogen by chlorine.

Compounds similar to the foregoing may be formed, in which bromine and iodine and even other substances are present in place of chlorine.

III. Compounds of Carbon and Oxygen.

A word on this subject is introduced here merely to complete the classification. The strict definition of organic compounds, given in another place, excludes the two compounds of carbon and oxygen. In fact, the latter are usually classified in the inorganic department.

Carbon forms but two compounds with oxygen, carbon monoxide, CO, and carbon dioxide, CO_2. The structural relation of carbon dioxide to marsh gas—the fundamental compound of organic chemistry—is very evident. In the one case, the four points of attraction of the carbon atom are satisfied by two atoms of oxygen ; and in the other case, by four atoms of hydrogen.

The small number of compounds of carbon and oxygen, as compared with the enormous number of compounds of carbon and hydrogen, is worthy of note.

Carbon dioxide is assumed to contain the radicle CO, called carbonyl.

The compound carbonyl chloride, $COCl_2$. is of theoretical interest. In it, a partial replacement of oxygen by chlorine is observed. The process corresponds with that whereby, in marsh gas, hydrogen is replaced by chlorine.

IV. Compounds of Carbon and Sulphur.

But one compound of these elements is known, carbon disulphide, CS_2. It is not usually considered as belonging to organic chemistry. It is a well known volatile liquid, and it is considerably used in the arts.

Its structural resemblance to carbon dioxide and thence to marsh gas, is easily apparent.

It is assumed to contain a compound radicle, CS, called thiocarbonyl. The compound, COS, called carbonyl sulphide, is of theoretical interest. It shows a partial substitution of sulphur for the oxygen in carbon dioxide, corresponding, in fact, to the substitution of chlorine for hydrogen in marsh gas already adverted to.

V. Compounds of Carbon and Nitrogen.

A very large number of compounds called cyanogen compounds or cyanides, are recognized as containing a radicle, CN, called cyanogen. The following list shows that this radicle acts like a monad element. Indeed, in many cases, its analogy with chlorine is very marked.

Hydrocyanic acid,	H(CN)
Cyanogen gas,	CN(CN)
Cyanogen chloride,	(CN)Cl
Cyanic acid,	HO(CN)
Thiocyanic acid,	HS(CN)

Theoretically, cyanogen compounds may be looked upon as connected with ammonia gas, NH_3. Thus, the group hydrocyanic acid, HCN, may be considered as ammonia gas, NH_3, in which three atoms of hydrogen are replaced by the triad radicle CH (called methenyl.)

Again, hydrocyanic acid, HCN, may be looked upon as marsh gas, CH_4, in which three atoms of hydrogen have been replaced by one atom of the triad element nitrogen.

Cyanogen compounds exist to some extent in nature. Thus, they are found in the kernels of certain fruits, like peaches. Most of such compounds, however, are produced by artificial processes. They have two great characteristic properties; first, many of them are poisonous—hydrocyanic acid, called prussic acid, being one of the most dangerous poisons known; second, they show a marked tendency to produce complex compounds and highly colored compounds, especially with metals, like iron and other members of its group—Prussian blue for example.

Certain cyanogen compounds are largely used in the arts. The most important are potassium cyanide, KCN, and potassium ferrocyanide, $K_4Fe(CN)_6$.

Their general mode of preparation involves the use of animal matters containing at once carbon and nitrogen. Such matters, when heated under proper conditions, undergo decomposition, certain elements being expelled, and the carbon and nitrogen entering into the new relations appropriate to the formation of cyanogen compounds.

Potassium ferrocyanide, $K_4Fe(CN)_6 . 3H_2O$. This is a very important salt in commerce, where it is known as *yellow prussiate of potash.* It is manufactured on a large scale by heating certain cheap animal matters, such as old leather or leather scraps, with potassium carbonate, K_2CO_3, and iron filings. The crude mass is cooled. Subsequently, it is treated with water. Thus, potassium ferrocyanide is brought into solution. The clear liquid is evaporated somewhat and then allowed to crystallize. Transparent yellow crystals of potassium ferrocyanide are thus produced.

This substance is largely used in the arts for the manufacture of potassium cyanide and also in the production of Prussian blue.

Potassium ferrocyanide, when added to ferric salts, gives rise, at once, to a deep blue precipitate called Prussian blue, $Fe_4Fe_3(CN)_{18}$. This compound does not dissolve readily in the presence of certain salts. When the latter, however, have been removed, it dissolves in pure water, imparting to it a deep blue color. On the large scale, Prussian blue is produced by the mixture of potassium ferrocyanide, ferrous sulphate, and chlorine water. Without the chlorine, ferrous salts afford a much lighter colored precipitate. The chlorine oxidizes the ferrous compound to the ferric form, and thus affords the deep blue precipitate.

When potassium ferrocyanide alone is subjected to the action of chlorine gas, a new compound, called potassium ferricyanide, $K_3Fe(CN)_6$, is produced.

Potassium ferricyanide is known as *red prussiate of potash.* With ferric salts, it gives only a brown discoloration ; but with ferrous salts, it gives a deep blue precipitate of soluble Prussian blue, $Fe_3Fe_2(CN)_{12}$, called Turnbull's blue. There are at least

three varieties of Prussian blue: the soluble blue, the insoluble blue, and Turnbull's blue. They vary in composition according to the method of preparation. They are very much used in the dyeing and printing of cotton goods. A tolerable blue on bleached cotton may be produced by dipping the bleached cotton cloth first, in solution of potassium ferrocyanide, and then in solution of ferrous sulphate, and, finally, exposing the goods to the oxidizing action of the atmosphere.

In certain kinds of calico printing, a paste is produced by mixing in water, potassium ferrocyanide, tartaric acid, and starch. The paste may be printed upon cloth. Then, upon heating, the acid decomposes the ferrocyanide, and Prussian blue is formed.

Potassium cyanide, KCN. This substance may be produced by heating potassium ferrocyanide either alone or with potassium carbonate.

It is a white salt having an odor somewhat resembling that of peach kernels. It is much used in certain operations connected with the processes of gold and silver plating by electrolysis. With certain salts of silver and gold, it forms double salts which are soluble and especially favorable for electro-deposition. It is largely used in extracting gold from certain low-grade ores.

It is also employed in the preparation of hydrocyanic acid, also called prussic acid.

Hydrocyanic acid, HCN. This substance, when in the anhydrous form, is a clear liquid which is extremely poisonous. With suitable metals, it forms a series of salts called cyanides.

It is an interesting fact that hydrocyanic acid is capable of production by the direct union of nitrogen and acetylene under the influence of a series of electric sparks. Since acetylene may be produced from its elements in similar fashion, it is plain that cyanogen compounds may be formed progressively from the elements composing them, and without the intervention of vital processes. This should be noted in connection with the fact that *ordinarily* cyanogen compounds are derived from potassium ferrocyanide which latter has been produced by the use of an organized substance, such as leather. The point just now presented is of considerable moment in connection with the whole theory of organic chemistry. It sustains the view now generally held, that it is likely to be found possible to produce all organic compounds except the organized ones from their elements without the intervention of the processes of living animals or plants.

Mercuric cyanide, $Hg(CN)_2$, is a white crystalline salt which may be produced by dissolving mercuric oxide, HgO, in hydro-

cyanic acid, HCN. The substance is interesting, partly on account of the fact that when it is heated, it gives off cyanogen gas.

Cyanogen gas, CN CN, is a colorless gas having an odor similar to hydrocyanic acid. It is distinctly poisonous. If the gas is allowed to escape from a small tube, it may be set on fire, whereupon it burns with a delicate pinkish-blue flame. If cyanogen gas is conveyed into a solution of potassium hydroxide in water, at least two salts are formed, potassium cyanide and potassium cyanate. Thus,

$$2(CN) + 2KOH = KCN + KOCN + H_2O$$

The operation is analogous to that whereby potassium chloride and potassium chlorate are formed, by the introduction of chlorine gas into potassium hydroxide solution.

Potassium cyanate, KOCN. This substance may be used for the preparation of cyanic acid, HOCN, and thence of ammonium isocyanate NH_4OCN. Upon allowing the latter to rest some time in water solution, it spontaneously decomposes into an isomeric substance, urea, HN_2CONH_2. This latter compound is very interesting on account of its relations to the history of theoretical chemistry. The distinguished German chemist, Friedrich Woehler, discovered this change in 1828; and his observation has ever since been noted as a most important historical event in chemistry. Urea had not been known previously except in the urine of the higher animals, produced therefore, by the influence of the vital processes; and moreover, the theory before Woehler's discovery was that organic compounds could not be produced artificially. The foregoing discussion on cyanogen has shown that the following synthetical operations are practicable.

Inorganic Synthesis of Urea.

A. Carbon and hydrogen may be made to unite directly to form acetylene, C_2H_2.

B. Acetylene and nitrogen may be made to unite directly to form hydrocyanic acid, HCN.

C. Hydrocyanic acid and mercuric oxide may be made to react so as to form mercuric cyanide, HgCN.

D.   Mercuric cyanide by heating yields cyanogen gas, CN·CN; this passed into potassium hydroxide solution yields potassium cyanate, KOCN.

E.   Potassium cyanate by action of dilute sulphuric acid may be made to yield cyanic acid, HOCN.

F.   Cyanic acid and ammonia may produce ammonium cyanate, NH_4OCN. (Note that while man's chief supplies of ammonia are derived from the decomposition of animal and vegetable substances, it may be produced without the intervention of the vital processes.)

G.   Ammonium cyanate may spontaneously turn into its isomer, urea.

While referring to cyanic acid, two important polymers should be mentioned.   They are

Cyanuric acid,	$H_3O_3(CN)_3$, and
Fulminic acid,	$H_2O_2(CN)_2$

Fulminic acid combines with metals to form highly explosive compounds.   Thus, mercuric fulminate, also called fulminating mercury, is the violent explosive used in percussion caps; and silver fulminate, also called fulminating silver, is a yet more dangerous explosive.

Thiocyanic acid, or sulphocyanic acid, HSCN, analogous to ordinary cyanic acid, is a substance of some interest.   It is considerably used in commerce in combination with the metals in the form of potassium sulphocyanate, KSCN, and ammonium sulphocyanate, NH_4SCN.   Both of these are white crystalline salts readily dissolving in water.   They are used as tests in chemistry. With very minute quantities of ferric salts, they produce deep blood-red colorations.

Mercury sulphocyanate, $HgS_2(CN)_2$, is a white powder which decomposing when heated yields a very voluminous mass of material.   Such material issuing from a suitable wrapper, produces the curious serpentine mass commonly known as Pharaoh's serpents. But the mercurial fumes evolved are noxious.

3

CHAPTER VI.

HYDROCARBONS.

Fatty Series; Aromatic Series.

The hydrocarbons are compounds containing carbon and hydrogen and nothing else. (They must not be confounded with carbohydrates.)

Hydrocarbons occur in natural gas, in petroleum, in ozokerite, in certain plants: india-rubber, turpentine, and certain essential oils are hydrocarbons. Certain hydrocarbons are readily produced by the decomposition of complex organic matters. Thus, peat, wood, bituminous coal, salts of organic acids, etc., generally produce hydrocarbons (as well as other compounds) when heated without free access of oxygen. (The process is called destructive distillation.)

The number of the hydrocarbons already known is very great — probably hundreds. Moreover their structure is such that it seems likely that many many more will be either discovered or produced hereafter.

Physically considered the hydrocarbons have certain general traits. Those having small numbers of carbon atoms are gaseous at ordinary temperatures; as the members having larger numbers are reached the substances are liquid; later members are solids.

Thus methane, marsh gas, CH_4, is a gas; nonane, C_9H_{20}, is one of the liquid constituents of kerosene oil; the constituents of paraffin wax, a solid, probably have at least as many as 20 atoms of carbon in the molecule.

Moreover as the number of carbon atoms increases there is apt to be a *definite rise in the melting and boiling points.*

The hydrocarbons are but slightly soluble in water.

Chemically considered the hydrocarbons are rather neutral and inactive. They act neither as acids nor alkalis. Certain powerful chemical influences affect them strongly, it is true; thus they burn in presence of oxygen and they are capable of chemical replacement of their hydrogen atoms, step by step, by various radicles, so as to give rise to an immense number of closely related compounds.

The formulas of the known hydrocarbons are such that these bodies naturally fall into groups called series — the formulas of all the members of a given series being expressible by one general formula.

In considering the hydrocarbons, as well as their derivatives, the bold distinction between the *fatty group* and the *aromatic group* must be carefully recognized.

General Formulas of Fatty Hydrocarbons.

1st series	C_nH_{2n+2}	paraffin series
2d series	C_nH_{2n}	olefine series
3d series	C_nH_{2n-2}	acetylene series
4th series	C_nH_{2n-4}	valylene series
5th series	C_nH_{2n-6}	di-acetylene series

The aromatic hydrocarbons, etc., will be considered later.

The following table including a number of the important hydrocarbons of the fatty series is worthy of attention :

TABLE — From Roscoe & Schorlemmer.

(C_nH_{2n+2})		(C_nH_{2n})		(C_nH_{2n-2})	
Methane,	CH_4	———		———	
Ethane,	C_2H_6	Ethylene,	C_2H_4	Ethine,	C_2H_2
Propane,	C_3H_8	Propylene,	C_3H_6	Propine,	C_3H_4
Butane,	C_4H_{10}	Butylene,	C_4H_8	Butine,	C_4H_6
Pentane,	C_5H_{12}	Pentylene,	C_5H_{10}	Pentine,	C_5H_8
Hexane,	C_6H_{14}	Hexylene,	C_6H_{12}	Hexine,	C_6H_{10}
etc.		etc.		etc.	

Structural Characteristics of Fatty Series.

The several series of hydrocarbons, and their allied compounds or derivatives, are characterized by several different methods of attachment of one or more pairs of carbon atoms.

In the *first series* of fatty hydrocarbons the method of attachment is evidently very simple. Every atom of carbon is attached to its neighboring atom or atoms of carbon by one point or attraction. The lowest member of this series may have one atom of carbon, the higher members may have many atoms of carbon, for example :

$$\begin{array}{ccccccc} & & & \text{H} & \text{H} & \text{H} & \text{H} \\ \text{Butane,} & C_4H_{10}, & \text{HC} & \!\!-\!\!\text{C} & \!\!-\!\!\text{C} & \!\!-\!\!\text{CH} \\ & & & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$$
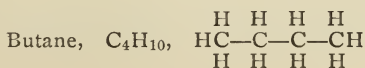
In the *second series* every member is characterized by this peculiarity: the first two carbon atoms are attached by two points of attraction in common. Necessarily then the lowest member must have at least two atoms of carbon. In the higher members of this series the first two carbon atoms are attached as described and then succeeding atoms are attached at one point of attraction as in the first series; for example:

$$\text{Ethylene,} \quad C_2H_4, \quad \overset{\displaystyle}{\underset{\displaystyle H \quad H}{HC = CH}} \qquad \text{Propylene,} \quad C_3H_6, \quad \overset{\displaystyle \quad\quad\quad H}{\underset{\displaystyle H \quad H \quad H}{HC = C—CH}}$$

In the *third series* there is this characteristic: the first two carbon atoms are attached by three points of attraction in common. Evidently in this series no lower member can exist th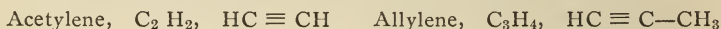an that having two carbon atoms. The higher members of the series are characterized by the first two carbon atoms united at three points of attraction each as stated, and the other carbon atoms attached by one point of attraction for each atom of carbon; for example:

$$\text{Acetylene,} \quad C_2 H_2, \quad HC \equiv CH \qquad \text{Allylene,} \quad C_3H_4, \quad HC \equiv C—CH_3$$

In the *fourth series* the linkage of carbon atoms is not definitely known; it is evidently more complex. For valylene, a member of this series, two rational formulas are suggested:

$$\text{Valylene,} \quad C_5H_6, \quad CH_2 = C(CH_3)—C \equiv CH \quad \text{or} \quad CH_3—CH = CH—C \equiv CH$$
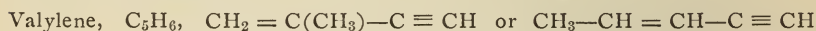
In the *fifth series* the characteristic method of linkage involves two pairs of carbon atoms, each pair being united by three bonds; for example:

$$\text{Di-acetylene,} \quad C_4H_2 \quad CH \equiv C—C \equiv CH$$
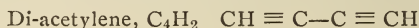
Evidently all the compounds of the five series of *fatty compounds* mentioned are *open chain compounds*. The members of the various *aromatic series* all tend to form closed chains.

Homologous and Heterologous Compounds.

The various hydrocarbons of a given series are called homologous compounds. Thus, ethane, propane, butane, are homologous. In a similar fashion the acids of this series, acetic acid, propionic acid, butyric acid, etc., are homologous to formic acid. In general a given series of carbon compounds may possess a large number of sets of homologues.

On the other hand, dealing with the compounds mentioned in another way, a set of substances having the same stem radicles but containing different *replacing* radicles may form a heterologous series. Thus from the radicle ethyl a heterologous series would include ethane, ethyl chloride, ethyl alcohol, ethylamine, acetic acid, etc.

In most cases each series is represented by many members, and these in turn are capable of forming many compounds with other elements or with other compound radicles. Thus, a given member of any homologous series may have one, two, or more (according to circumstances), of its hydrogen atoms replaced by chlorine, bromine, or other elements, or by a proper number of monad radicles; or again, in certain cases, two atoms of hydrogen may be replaced by one atom of oxygen or of sulphur; while in other cases, three atoms of hydrogen may be replaced by one atom of nitrogen or of arsenic or of antimony or of phosphorus, as the case may be. Sometimes several substitutions or combinations may take place at once. Thus, a given hydrocarbon may be looked upon as a kind of trunk from which branches may be extended, thus giving rise to very complex molecules.

The following table is worthy of attention as showing corresponding compounds of the fatty series:

Table of a few Fatty Derivatives: Paraffin Series.

HYDROCARBONS.	CHLORIDES.	ALCOHOLS.	AMINES.	ACIDS.
Methane, $CH_3\,H$	Methyl chloride, $CH_3\,Cl$	Methyl alcohol, $CH_3\,OH$	Methylamine, $CH_3\,H_2\,N$	Formic acid, $CH_2\,O_2$
Ethane, $C_2\,H_5\,H$	Ethyl chloride, $C_2\,H_5\,Cl$	Ethyl alcohol, $C_2\,H_5\,OH$	Ethylamine, $C_2\,H_5\,H_2\,N$	Acetic acid, $C_2\,H_4\,O_2$
Propane, $C_3\,H_7\,H$	Propyl chloride, $C_3\,H_7\,Cl$	Propyl alcohol, $C_3\,H_7\,OH$	Propylamine, $C_3\,H_7\,H_2\,N$	Propionic acid, $C_3\,H_6\,O_2$
Butane, $C_4\,H_9\,H$	Butyl chloride, $C_4\,H_9\,Cl$	Butyl alcohol, $C_4\,H_9\,OH$	Butylamine, $C_4\,H_9\,H_2\,N$	Butyric acid, $C_4\,H_8\,O_2$
Pentane, $C_5\,H_{11}\,H$	Pentyl chloride, $C_5\,H_{11}Cl$	Pentyl alcohol, $C_5\,H_{11}OH$	Pentylamine, $C_5\,H_{11}H_2\,N$	Pentylic acid, $C_5\,H_{10}O_2$
Hexane, $C_6\,H_{13}\,H$	Hexyl chloride, $C_6\,H_{13}Cl$	Hexyl alcohol, $C_6\,H_{13}OH$	Hexylamine, $C_6\,H_{13}H_2\,N$	Hexylic acid, $C_6\,H_{12}O_2$

The members in an up and down line form a homologous series; the members in a right and left line form a heterologous series.

CHAPTER VII.

FATTY HYDROCARBONS

Of the Paraffin Series, $C_n H_{2n+2}$.

The hydrocarbons of this series have the general formula C_nH_{2n+2}. The first member of the series is marsh gas, also called methane, CH_4. The other members have higher formulas with 2, 3, 4, . . . n atoms of carbon, then such number of atoms of hydrogen, as accords with the demands of the general formula. The following list presents the names and formulas of some of the best known hydrocarbons of this series:

General formula, C_nH_{2n+2}		Boiling points.	Melting points.
Methane,	$C H_4$	gaseous.	
Ethane,	$C_2 H_6$	gaseous.	
Propane,	$C_3 H_8$	gaseous.	
Butane,	$C_4 H_{10}$	$1°C.$	
Pentane,	$C_5 H_{12}$	36	
Hexane,	$C_6 H_{14}$	69	
Heptane,	$C_7 H_{16}$	9S	
Octane,	$C_8 H_{18}$	125	
Nonane,	$C_9 H_{20}$	150	
Decane,	$C_{10} H_{22}$	173	
Undecane,	$C_{11} H_{24}$	195	
Dodecane,	$C_{12} H_{26}$	215	
Tridecane,	$C_{13} H_{28}$	234	
Tetradecane,	$C_{14} H_{30}$	253	$5.5°$
Pentadecane,	$C_{15} H_{32}$	271	10.
Hexdecane,	$C_{16} H_{34}$	solid at ord. temp.	20.

Additional compounds are known in regular order (with few exceptions) from the compound with C_{17} up to that with C_{35}. The compound $C_{60}H_{122}$ is also known.

From the compound with C_{16} upward the hydrocarbons are waxy solids at ordinary temperatures.

The table gives rise to the following suggestions :

First. It is tolerably complete as far as it goes. Probably, higher compounds of the series may be discovered hereafter. Probably, also, omitted members may be discovered.

Second. The consecutive members differ from one another by the addition of CH_2.

Third. They illustrate one of the general laws of chemical philosophy, namely, the more atoms in the molecule, the higher the melting point or boiling point ; the less number of atoms in the molecule, the greater the volatility or tendency to assume the gaseous condition.

Fourth. The addition of the group CH_2 to a given substance tends to raise its boiling point about twenty or thirty degrees.

Fifth. The ordinary structural formulas are represented by the diagrams given below :

First Member	Second Member	Third Member	Fourth Member
H	H H	H H H	H H H H
HCH	HC—CH	HC—C—CH	HC—C—C—CH
H	H H	H H H	H H H H
CH_4	$CH_3 \cdot CH_3$	$CH_3 \cdot CH_2 \cdot CH_3$	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$
Methane	Ethane	Propane	Butane

Sixth. Each member of the series is viewed as made up of a compound radicle united with one atom of hydrogen. Thus, methane, CH_4, is viewed as methyl hydride, CH_3H ; and in subsequent formation of other compounds, the methyl, CH_3, is believed to hold together as a compound radicle, and as such to be capable of transfer from one compound to another. Similarly, ethane, C_2H_6, is viewed as composed of ethyl, C_2H_5, united with H. Then, ethane, C_2H_6, is ethyl hydride, C_2H_5H. The view here expressed is not based upon a mere mechanical or imaginary subdivision of the formulas. It is, rather, a substantial and well based induction formed after a careful study of organic compounds.

All study of the hydrocarbons of this series sustains the conclusion that they are *open chain* compounds ; but they are not necessarily in all cases as simple in their plan of construction as represented in the diagrams given.

Isomerism in the Paraffin Series.

1.   Probably, the composition of *marsh gas* is correctly repre-
sented as having one atom of carbon and four atoms of hydrogen
somehow arranged about it.

If the four atoms of hydrogen are practically identical in prop-
erties, so that it is impossible to distinguish one from another, a
change in their relative positions will be of no moment as
respects the properties of marsh gas.

If in a given molecule of a marsh gas, having the formula CH_4,
every atom of the substance designated by H differs appreciably
from every other atom of the thing so designated present in that
molecule, then two geometrical isomers of the compound become
possible.

As a matter of fact no isomers of marsh gas have yet been
recognized.   Moreover at present the atoms of hydrogen are not
distinguishable one from another.

While the *general* view presented by the formula of marsh gas is correct, it
gives rise to some misconception from the fact that the atoms are represented
as arranged in a *plane*.   Modern views of chemical molecules have led to the
belief that different parts of a given molecule may lie in different planes.   Even
in a case like marsh gas, it has been assumed that the four points of attraction
of the atom of carbon, instead of lying in one plane, may really have positions
more properly represented by the four solid angles of a tetrahedron.

2.   Next consider *ethane.*   If its formula is constructed, gen-
erally speaking, on just principles, no considerable modification
is possible, except upon those stereo-chemical grounds already
alluded to.   As a matter of fact, ethane has not yet been proved
to produce isomers.

3.   A consideration of the substance *propane* shows that, in the
view now taken, isomers are impossible.   The three atoms of car-
bon must be considered as standing, one in the middle position
and one at either end.   Now so long as the different carbon
atoms are practically identical and the different hydrogen atoms
are practically identical, no isomers can be expected.   None
have yet been recognized.

4.   When, however, *butane* is considered, it is easily seen that
isomers may be formed.

Thus, there are at least two ways of writing the rational formula for butane, and both of them in accordance with the general open chain system of this series.

First Method

H   H   H   H
HC—C—C—CH
H   H   H   H
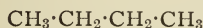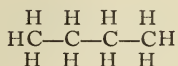
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$
Normal butane

Second Method

H
HCH
H | H
HC——C——CH
H   H   H
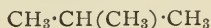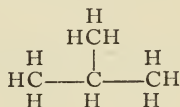
$CH_3 \cdot CH(CH_3) \cdot CH_3$
Isobutane

In normal butane, we have simply the four atoms of carbon arranged in a row. In isobutane, we have first, three atoms of carbon arranged in a row ; and then, instead of the fourth atom of carbon being placed at one end of the series, it is attached to the middle atom of the series and as a side branch. The particular side of the middle atom, to which it is attached, makes no difference.

As a matter of fact, it is found that two kinds of butane can be produced, and they are designated as normal butane and isobutane, respectively.

5. It has been said already that as the hydrocarbons advance in their number of carbon atoms, the numbers of isomers theoretically possible rapidly increase. Experiments sustain the theory.

When the next number of the series, that is, *pentane*, is examined, it is found that theoretically three isomers are possible. As a fact, three, and only three, have been found.

First Method

H   H   H   H   H
HC—C—C—C—CH
H   H   H   H   H
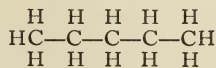
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$
Normal pentane

<pre>
        Second Method   Third Method
             H   H
            HCH   HCH
        H | H   H   H | H
        HC—C—C—CH   HC—C—CH
        H   H   H   H   H | H
                                         HCH
                                          H
</pre>

<div align="center">

$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH_3$ $C(CH_3)_4$
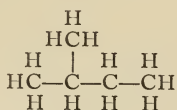
Isopentane or Dimethylethyl methane   Tetramethyl methane
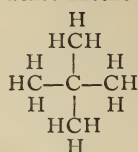
</div>

A Few Individual Hydrocarbons of this Series.

Methane, or methyl hydride, CH_4, *also called marsh gas.* This substance sometimes emanates from crevices in coal mines. It often accompanies petroleum as it issues from the earth. It also forms a part of the combustible gas produced by gas wells and named in general *natural gas.* It is a constituent of the illuminating gas manufactured from soft coal.

Marsh gas is ordinarily prepared by heating sodium acetate $NaOOC \cdot CH_3$, with sodium hydroxide, $NaOH$.

$$\left. \begin{matrix} Na \\ OC \cdot CH_3 \end{matrix} \right\} O \;\; + \;\; \left. \begin{matrix} Na \\ H \end{matrix} \right\} O \;\; = \;\; \left. \begin{matrix} Na_2 \\ CO \end{matrix} \right\} O_2 \;\; + \;\; CH_4$$
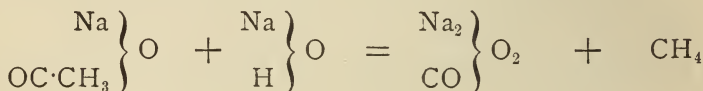
This may be called an analytical method rather than a synthetical. Thus, the methane is obtained by breaking down the more complex acetic molecule; and yet further, this acetic molecule was obtained by the breaking down of the more complex cellulose molecule. (Acetic acid is produced by the destructive distillation of wood.) But one of the chief aims of the organic chemist is to produce organic compounds — the more complex the better — from their constituents used in the elementary form, that is, to produce organic compounds by the employment of chemical forces alone without the intervention of the vital processes of animals and plants. So it comes about that chemists have made efforts to produce marsh gas from carbon and hydrogen. The effort has been successful, and it is the more interesting because methane is looked upon as a sort of a fundamental nucleus of organic compounds.

Ethane, or ethyl hydride, C_2H_6. This substance, the second hydrocarbon of the paraffin series, is ordinarily a gas. By cold and pressure, however, it may be reduced to a liquid. It occasionally exists in nature in the " natural gas " evolved by gas wells. Ethane also exists in Pennsylvania petroleum dissolved in the liquid hydrocarbons.

Ethane may be produced by a number of different methods. Theoretically, one of the most interesting is that whereby it is produced from methyl iodide and zinc in a closed glass tube.

$$2CH_3I + Zn = 2CH_3 + ZnI_2$$
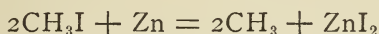
The action shows that two molecules of methyl are produced ; but as a matter of fact, when the experiment is performed, the two molecules of methyl consolidate to form one of ethane.

$$2CH_3 = C_2H_6$$
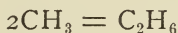
Propane, or propyl hydride, C_3H_8. This substance occurs in petroleum. It is a colorless gas of no considerable practical importance.

Butane, or butyl hydride, C_4H_{10}. This substance is a colorless gas. Like most of the members of the paraffin series, it occurs in petroleum. It may be produced, however, by a variety of chemical reactions. Like the foregoing hydrocarbons, also, it is capable of producing a large number of substitution compounds. It is viewed as containing a radicle, butyl, C_4H_9; which radicle, combining with halogens, with hydroxyl, amidogen, etc., gives rise to a set of compounds corresponding to many already described. Thus, it forms butyl ethers, butyl alchohols, butyl iodides, butyl esters, butyric acids, butyl amines.

It must be borne in mind, however, as was previously stated, that the larger number of carbon atoms in butane affords opportunity for isomers.

Normal pentane, C_5H_{12}. This substance is a volatile liquid. It exists in petroleum. It is produced artificially in the distillation of cannel coal for the manufacture of illuminating gas. It is assumed that pentane contains a hydrocarbon radicle, pentyl, C_5H_{11}. Like members of preceding groups, it affords a large number of derivatives. Of course, owing to its number of atoms of carbon, it forms a larger number of isomers than the foregoing compound.

Normal hexane, C_6H_{14}. This is also a liquid. It exists, like many of the higher hydrocarbons of this series, in petroleum and in the products of the distillation of cannel coal. As has

been intimated before, there are five possible isomers, all of which have been produced and studied. Of course, they give rise to various alcohols and ethers, acids, and other derivatives, also capable of forming isomers.

This series has a great many members with higher numbers of carbon atoms, but they need not be discussed here.

Fatty Hydrocarbons of the Olefine Series, $C_n H_{2n}$.

The olefines form an important natural series of which many members are known. From the compound having C_2 up to the compound having C_{30} the list of known compounds is nearly complete. Below are the names and formulas of a few of them:

Olefines, $C_n H_{2n}$

Ethylene,	C_2H_4	Octylene (caprylene),	$C_8 H_{16}$
Propylene,	C_3H_6	Nonylene,	$C_9 H_{18}$
Butylene,	C_4H_8	Dekylene,	$C_{10}H_{20}$
Amylene (pentylene),	C_5H_{10}	Undekylene,	$C_{11}H_{22}$
Hexylene,	C_6H_{12}	Duodekylene,	$C_{12}H_{24}$
Heptylene,	C_7H_{14}	Tridekylene,	$C_{13}H_{26}$

Many isomers are known.

1. They all have this structural characteristic (already referred to) viz., in each substance is one pair of carbon atoms held together by a double bond; additional carbon atoms, if any, being held by a single bond. Thus they are unsaturated compounds.

2. The olefines exist in certain petroleums, especially that of Russia and Burma (only in small quantity in American).

The olefines are produced artificially from certain other carbon compounds—by destructive distillation, for example.

3. As might be expected, the lower members of the series are gases at ordinary temperatures; the higher members are solids; the intermediate members are liquids.

4. The olefines are more active chemically than the paraffins; a fact due to the double linkage.

One important feature is the ease with which they take on bromine (and indeed other chemical substances), thus loosing the double bond.

Of course, they burn with luminous flame.

Ethylene, C_2H_4. This is a colorless gas. It is produced by the dry distillation of many organic substances, as in the manufacture of illuminating gas from cannel coal—indeed, it is a very valuable constituent of the gas, because it affords much light.

Ethylene is also produced when sulphuric acid acts upon alcohol.

Ethylene may be obtained by the direct combination of acetylene, C_2H_2, with hydrogen, under the influence of the electric current.

Ethylene is capable of affording substitution products containing chlorine and other halogens. It affords also a very large number of other compounds corresponding in a general way with the organic salts, nitrogen bases, phosphorus bases, etc., already shown to be produced from methane and ethane.

Fatty Hydrocarbons of the Acetylene Series, C_nH_{2n-2}.

Many acetylenes are known.

They form four subordinate series of which two are worthy of mention here. In the one set a given molecule having three carbon atoms may have them attached by *one bond and three bonds*, as in the first allylene, C_3H_4, composed as follows, $H_3C \cdot C : CH$. In the other set there may be *two bonds and two bonds*, as in the second allylene, C_3H_4, composed as follows, $H_2C : C : CH_2$.

Acetylenes are known from the member having C_2 to that having C_{20} with but few gaps in the list.

One important chemical characteristic of the *one-three* acetylenes is their tendency to combine with metallic compounds, especially those of copper and silver. Thus, the first acetylene, C_2H_2, forms copper acetylene, $C_2H_2Cu_2O$ and silver acetylene, $C_2H_2Ag_2O$, both of which are explosive, as might be expected.

Naturally the acetylenes burn, and with smoky flame.

The first member, from which the series is named, is itself called acetylene.

Acetylene, C_2H_2, is a colorless gas possessing a peculiar and disagreeable odor.

1. It exists in minute quantity in illuminating gas. It may be produced by a variety of decompositions of organic com-

pounds, such as by passing vapors of methyl alcohol, ethyl alcohol, ethyl ether, etc., through red hot tubes.

2.   An interesting method of producing acetylene is that discovered by Berthelot and already referred to on preceding pages ; that is, by conveying an electric current, flowing as an arc from carbon poles, through an atmosphere of hydrogen. (It should be observed that the electric spark from an induction coil decomposes acetylene.) Under the prescribed conditions, the carbon and the hydrogen unite, forming acetylene. This process has been referred to before as the first step in many organic syntheses.

3.   Acetylene may be readily prepared by action of water on calcium carbide, CaC_2. (The calcium carbide is formed by the action of an arc light electric current on a mixture of lime or chalk and powdered coal.)

$$CaC_2 + 2H_2O = CaO_2H_2 + C_2H_2$$
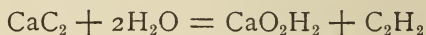
This important method has of late received much attention, for it is believed to be a cheap process. As acetylene, when burned in air, affords a very brilliant light, it is thought by some that the process under discussion may have important commercial applications.

Isoprene, C_5H_8, is a liquid produced by decomposition of caoutchouc and by passing vapor of turpentine, $C_{10}H_{16}$, through a red hot tube. Isoprene upon exposure to light changes slowly into a caoutchouc similar to that of india rubber. If this process can be practically applied, it may become of great importance to the rubber industries.

Fatty Hydrocarbons of the Valylene Series, C_nH_{2n-4}.

These are open chain compounds with a special carbon linkage. It may be illustrated by the constitution of the first compound known, valylene, C_5H_6, whose structure is believed to be represented by the expression, $H_2C : C(CH_3) . C : CH$ or by $H_3C \cdot CH : CH \cdot C : CH$.

But few members of this series have been studied.

Fatty Hydrocarbons of the Diacetylene Series, $C_n H_{2n-6}$.

These are open chain compounds. The first member, diacetylene, C_4H_2, is believed to have the constitution expressed by $HC:C \cdot C:CH$.

But few members of this series have been studied.

This last fatty series must be carefully distinguished from the important *aromatic hydrocarbon series*, called the benzene series, having the same general formula, $C_n H_{2n-6}$.

CHAPTER VIII.

FATTY HYDROCARBONS.

Petroleum, Etc.

Introduction. Petroleum flows from the earth as a mixture of oil, gas, salt water, and sand. When it subsides in a hollow, the sand and water fall to the bottom, the gas partly escapes into the air, while the oil is drawn off by pipes to the refinery.

Chemical Composition. American petroleum consists mainly of hydrocarbons of the paraffin series, C_nH_{2n+2}. In addition, it sometimes has olefines, C_nH_{2n}, and occasionally aromatic hydrocarbons, C_nH_{2n-6}. In some cases sulphur compounds are present.

Occurrence. Petroleum has been found in rocks of all geological ages. But it occurs principally in those of the Silurian age—the age of mollusks, and in those of the Devonian age—the age of fishes. Speaking mechanically, there seem to be necessary first, an original source of oil; above this a stratum of sand which shall hold the oil as in a sponge; above this an impervious stratum, as of shale or clay, which shall act as a sort of cover to prevent the escape of the oil. It is generally admitted that the oil *ascends from below* into the sands holding it.

Sources. The world's supply of petroleum comes principally from the United States and Russia, but the following localities are worthy of mention:

Austria, Germany, Italy; Canada; Japan; Burma and India; Peru, the Argentine Republic, Equador.

(The oil produced by the distillation of bituminous material, in Italy, France and elsewhere should not be confounded with that derived from supplies of oil ready-formed in the earth.)

The United States afford about $\frac{5}{6}$ of the present output of crude oil; Russia about $\frac{1}{7}$; Canada and Austria about $\frac{1}{70}$ each.

The world's output of crude oil, per annum (in barrels of 42 gals. each):

United States, about	.	.	.	48,000,000 bbls.
Russia,	"	.	.	.	8,000,000 "
Austria,	"	.	.	.	800,000 "
Canada,	"	.	.	.	750,000 "

It is considered not improbable that the region about the Mackenzie River may prove to be one of the most productive areas.

In the years 1894-5 there has been a decided decline in production in the older fields of the United States — accompanied, however, by an increase in the case of newer fields.

Petroleum districts of the United States. First, the Appalachian field (embracing western Pennsylvania and New York, West Virginia, and eastern Ohio.)

This is at present the one furnishing the largest amount of oil. Its area is about 500 square miles. The Pennsylvania portion includes: (a) the Allegheny districts, (b) the Bradford district, (c) the Warren district and the Forest district, (d) the Venango district; this has proved one of the four most productive counties, perhaps it already heads the list, (e) the Butler district, (f) the Beaver district; in Beaver County a very valuable oil has been found, different in quality, and generally of a higher grade than that produced elsewhere, (g) the Washington district. The oils of these districts vary considerably in their consistency and in their chemical constitution, but they do not yield sulphur oils as some of the other fields do.

Second, the Limestone field (embracing the Lima district of western Ohio and Indiana.) This affords a dark-colored and strongly sulphuretted oil. It commands a relatively lower price, owing to the expense involved in the removal of the sulphur.

Third, the Florence field of Colorado. Probably the yield of oil will be much increased in the future.

Fourth, the Southern California field. Here also there are evidences of increased production.

Fifth, the Kentucky field. The yield has been thus far small, partly on account of the cost of transportation to the refinery.

Sixth, the Wyoming field. The oil is of superior quality and capitalists are now engaged in preparations for large developments.

Production of crude petroleum in the United States for the year 1894:

Pennsylvania, New York, and West Virginia, about .	30,600,000 bbls.
Ohio and Indiana, about	16,500,000 "
Colorado, about	800,000 "
California, about	600,000 "
Kentucky and Tennessee, about . . .	1,000 "
Wyoming and other States, about . . .	2,700 "
	48,503,700 "

The American oil deposits, already proved by boring, are said to represent an area of over 200,000 square miles.

Oil has been struck at from 50 to 100 feet in depth, while in other cases it has required boring to 1,000 feet, or even to 3,000 feet.

History of American petroleum. The North American Indians appear to have been familiar with petroleum oil as recognized on the surface of certain pools. At first this oil was employed in a crude condition as a medicinal agent under the name of Seneca oil. In certain places the whites gathered the oil by saturating flannels with it, later wringing out the oil from the flannel.

In 1833 Professor Benjamin Silliman, Sr., in an article in the *American Journal of Science*, describes the celebrated oil spring of the Seneca Indians, near Cuba, N. Y. He says "they collected petroleum by skimming it like cream from the milk pan;" he adds that "the oil is thick, adhesive, and of foul appearance, like very dirty tar or molasses, but that it is purified by heating it and straining it while hot through flannel or other woolen stuff." Further he states that "the people in the vicinity use it for sprains and rheumatism, rubbing it upon the part affected." Apparently the petroleum used in the Eastern States under the name of Seneca oil did not come from the spring described, but from a point about one hundred miles from Pittsburg called Oil Creek, in Venango County.

The great success of James Young and others in making oil by distillation from bog-head coal and from shales, in Scotland, led to an attempt to make oil from similar materials in the United States. At first such oil was distilled from Albert coal, a kind of asphaltum obtained in New Brunswick. A good lubricating oil was made in this way. Later, oils were manufactured from the rich cannel coals of Virginia and Kentucky. In the neighborhood of the year 1855 oil was discovered at Tarentum, not far from Pittsburg, by men who were boring a well for salt brine. These oils, although obtained in small quantities, were used for medical purposes, for burning, and for lubricating. In 1854 a company of Eastern gentlemen became interested in petroleum and one of them suggested boring as a means of obtaining oil in larger quantities. They engaged Professor Silliman of Yale College to give some of their oil a careful examination. He stated that in his opinion " it contains a large proportion of benzole and naphtha, and that it will be found more valuable for purposes of application to the arts than as a medicinal, burning, or lubricating fluid." Thereupon the company secured 105 acres of land near the junction of Pine and Oil Creeks, and they engaged the notable Col. E. L. Drake to go out to Titusville and drill an artesian well for oil. Drake appears to have worked through the season of 1858 and a part of 1859 under many difficulties; but in August,

1859, he obtained a small amount of petroleum. His was the first petroleum well artificially drilled. Considerable excitement was created by the success or this well. It was followed by the permanent development of a considerable territory away from that principal centre. Wells were bored in various regions where it was found oil could *not* be obtained, extending along the Allegheny River, and, later, into Ohio and West Virginia.

In 1860 the interest in Pennsylvania over the finding of oil was intense. It led to a period of excitement surpassed only by that of the California gold fever. Pithole City in 1865 had the largest post-office, except Philadelphia, in Pennsylvania. But it is now a place of no consequence.

During the first two years of success, the search for oil was restricted to the territory around Titusville; later, wells were struck on the Allegheny River with abundant success. During this time oil was pumped; but in February, 1861, a flowing well was struck which yielded 300 barrels a day, and which continued to flow for fifteen months. Before the surprise and interest incidental to this discovery had expended itself, the Phillips well was struck, yielding about 3,000 barrels a day. Other wells of almost equal productiveness were later secured.

Boring the wells. The oil is obtained at varying depths. Thus some of the wells of West Virginia and Ohio are only 60 or 80 feet deep, while some of those in Pennsylvania (Washington County) are 2,600 feet deep. It is frequently the case that new wells yield oil without pumping; they are called flowing wells or "gushers." The flow seems to be due to the pressure of gas, which, little by little, escapes, so that eventually, all wells have to be pumped. It is stated that the average production of above 24,000 wells actually at work in Pennsylvania in 1886 was a little short of three barrels per day.

Wells are drilled in the United States by the use of extremely ingenious appliances. The simplest is a heavy chisel attached to a long rope. By means of a derrick the chisel is raised and dropped; from time to time the tools are withdrawn, a small quantity of water is poured into the well, then a pump is applied to bring to the surface pulverized material from which the nature of the strata attacked may be determined. Sometimes when a deep well fails to yield petroleum, or yields but little, the process called "shooting" is employed. A water-tight torpedo charged with nitro-glycerine is lowered into the well, water is allowed to fill the well, then the torpedo is exploded by electricity or otherwise. As a result the flow of oil is generally increased.

In connection with petroleum wells some curious circumstances may be worthy of mention, even though thought incredible. In Venango county,

Pennsylvania, a well called " the Sunday well," is said never to have yielded a crop of oil except on the first day of the week. Another curious well called " the lunatic oil spring," is said to begin to flow oil when the new moon appears, increasing in volume as the moon grows. When the moon is full the spring yields about three barrels of oil every day, the yield decreasing and increasing with the phases of the moon.

Transportation of oil. The early method of transportation of oil was by the use of barrels. At present, oil is transported not only by tank cars, but also by 6-inch pipe lines, which receive their supply of oil from immense tanks near the wells. The pipes extend to Cleveland, Chicago, Philadelphia, Brooklyn, Baltimore, and Buffalo, aggregating 2,500 miles. They lie but a short distance under ground, and they are constantly patrolled by watchers for leaks ; in many places these men have worn paths miles in length, so that it is very easy to trace the course of the pipes. In connection with the pipe lines, ingenious pumps and other scientific devices are used. The oil is forced along steadily over hills and under rivers until it is delivered at the proper point. Any individual owning a well may deliver oil at tanks near by, and then receive at once a pipe line certificate for the proper number of barrels of oil. The certificates are bought and sold freely, so that the producer of the oil virtually receives his pay at once.

Occasionally tanks have been struck by lightning and the oil set on fire. In such cases the oil may burn at the top for a short time without serious damage; the unburned oil beneath may be drawn off and saved. In the early history of tanks a cannon ball was sometimes fired at the lower part of the tank so as to make a hole and let the unburned oil run into a depression of the earth near by, from which it could be subsequently recovered. At present great care is taken to protect tanks by lightning rods, as well as by safety valves. These latter may accommodate the expansion of the oil incidental to hot weather.

Illuminating oil may be shipped in tank steamers or in tin cans. Such large numbers of cans are used that incidentally, the industry of their manufacture is a large and important one.

A singular accident is narrated as having occurred in Wisconsin in the night. Some cars were thrown from the track; two of them contained naphtha, and the liquid spread over a marsh near by. A boy living in the vicinity came toward the wreck with an open lantern. The naphtha became ignited, the cars were consumed, one of the railroad men was burned to death, others escaped only by jumping into the lake near by.

Fractional distillation of crude oil. As the oil comes from the well it is usually mingled with salt water. After standing

awhile the salt water falls to the bottom of the mixture and may be drawn off. Next the oil goes to the refinery. There it is at first heated in large kettles practically retorts; the oil liberates vapor; the vapor passes through condensers and forms gasolene or naphtha. As the heating proceeds, oils of greater density distil, and these being collected in other reservoirs, are used for the manufacture of illuminating oil. By and by, heavier oils suitable for lubrication are obtained; these oils are often spoken of as paraffin oils. From these heavier materials also the substance known as vaseline is produced.

The residuum in the still is of tarry consistency and may be used mixed with fine coal, or otherwise, as fuel.

The amount of illuminating oil obtained is increased by the process called "cracking." This is a form of destructive distillation, rather than of fractional distillation. A heavy lubricating oil when dropped into a still containing heavy oil highly heated becomes itself decomposed, and yields vapors of illuminating oil. Thus the fractional distillation of Pennsylvania petroleum which ordinarily gives about 40 per cent. of illuminating oil and 25 per cent. of lubricating oil, may, by the process of cracking, be made to yield 75 per cent. of illuminating oil and about 6 per cent. of lubricating oil.

In obtaining paraffin, the heavy oil from the still is cooled by refrigerating machines, and the pasty solid is subjected to the action of a hydraulic press. Later the paraffin is remelted and filtered through bone coal, in order to decolorize it.

Certain of the distillates from the heavier portions of oil are refined by filtration and otherwise, and then form a material known as vaseline.

The commercial products of American petroleum may be defined chemically as follows : The light group, including petroleum ether, etc. ; chiefly pentane, C_5H_{12}, hexane, C_6H_{14}(C_6H_{12} also present), heptane, C_7H_{16}(C_7H_{14} also present).

The petroleum spirit group ; chiefly heptane, octane, nonane.

The burning oil group ; chiefly decane, undecane, dodecane.

The paraffin wax group ; higher hydrocarbons, containing from C_{20} to C_{27}.

The following are a few of the products of petroleum :

Cymogene. It boils at 0 C. It is used in the manufacture of artificial ice.

Rhigolene. It boils at $18\frac{3}{10}$ degrees C. It is used as an anasthetic.

Petroleum ether. It boils at from 70 to 90 degrees C. It is used as a solvent for caoutchouc and also in gas machines.

Gasolene. It boils at 70 to 90 degrees C. It is used in extracting oil from seeds and also in gas machines.

Naphtha. It boils at from 80 to 110 degrees C. It is used in vapor stoves and street lamps. It is also employed as a solvent for resins.

Ligroine. It boils at from 80 to 120 degrees C. It is used for burning in sponge lamps.

Benzine. It boils at from 120 degrees to 150 degrees C. It is used as a substitute for turpentine.

Burning oil or kerosene. It is used in kerosene lamps. It varies as to fire test from 110 degrees Fahrenheit to 150 degrees Fahrenheit.

Lubricating oils. These oils are the heavier ones as found in nature, or else they are the residue from the fractional distillation of crude oils.

Refining burning oil. In refining illuminating oil the portion of the distillate suitable for this purpose is placed in large tanks and agitated with $1\frac{1}{2}$ to 2 per cent. of sulphuric acid, the agitation being accomplished by air which is forced into the tank. When the sulphuric acid has done its work the mixture is allowed to subside, the oil coming to the top. This is drawn off and washed with water and a solution of sodium carbonate, the latter to remove final traces of acid. The acid becomes deeply colored. It is charged with sulpho-compounds of the olefines, while SO_2 escapes. The *sludge acid* is used for certain inferior purposes, for example, in the manufacture of fertilizers (especially for acting on insoluble phosphates with a view of turning them into the soluble form.)

In refining sulphur oils like the Lima oils, metallic copper or powdered copper oxide or a solution of lead oxide in sodium hydroxide is often employed, the intention being, of course, to withdraw sulphur. The sulphur oils are objectionable because they have a very offensive odor.

Russian petroleum. The Russian oils come from two districts, one at either extremity of the Caucasus Mountains. The western district is on the Black Sea, near the Kouban River. The eastern district is on the Peninsula of Apsheron, extending into the Caspian Sea, and including the city of Baku.

Although the existence of petroleum (and especially the gaseous vapors associated with it) has long been recognized in the

neighborhood of the Caspian Sea, the extensive development of the Russian petroleum industry has been since about 1860. Up to 1872, petroleum in Russia was a State monopoly. At the present time, about one-half of the petroleum grounds belong to private owners.

The extent of Russian territory in the Caucasus capable of yielding oil is very great. Commencing with a point on the Taman Peninsula projecting into the Black Sea on its northern boundary, a line drawn on the map in a southeasterly direction to Baku on the Caspian Sea, represents a distance of about 1,500 miles. This line traverses the oil belt. Its width has not been accurately determined, but if ten miles is taken as a minimum estimate, the area represents 15,000 square miles. In many parts of the region sketched, ample quantities of oil have been found.

In the Baku region, the oil belt, instead of being ten miles in width, previously assumed as an average, is in fact about 200 miles in width. This district has already 750 oil wells in operation, practically all of these yielding without signs of exhaustion, notwithstanding the fact that immense loss is constantly caused by lack of experience in dealing with the product. Professor Mendeléeff, who visited Baku in 1882, declares that, all things considered, these oil wells have no parallel in the world, and that the general district referred to is not only more productive than any other now known, but it is also more extensive.

The chief commercial development, however, has taken place in the region about Baku. This has been largely due to the convenient railroad transportation to Batoum, on the Black Sea, from which point the principal European points are easily reached by water. The development of the petroleum trade of the Caucasus is largely due to the Nobel Brothers. They started business at Baku in 1874, and in the following year undertook the production of petroleum on a small scale. At that time native merchants were handling oil in primitive ways, using carts and leather bottles. Overcoming great difficulties, the Nobel Brothers brought experts from the United States, and by introducing pipe lines, storage tanks, tank cars, tank boats, they soon built up an enormous business. In 1887 the Paris house of Rothschilds undertook the petroleum business in the Caucasus and soon surpassed Nobel Brothers.

Next to the Baku region, the districts of Fer and Tiflis are worthy of mention. In this vicinity oil is found in abundant quantities, and it has been used for ages.

The Baku wells are sufficiently elevated above the harbor and the refineries to allow the oil to reach these points by gravity. About 400 wells are crowded together in this neighborhood, in the space of not more than three miles square. The deepest well yet sunk in this locality is only about 825 feet, while oil is often reached in paying quantities at a depth of 100 feet.

The Balakhany field is about eight miles from the town of Baku. This district covers the area of about four square miles. The chief source of oil is the Bibieibat field, which is about three miles south of Baku.

The celebrated Droojebah well : When oil was first struck, the well threw out as much oil in one day as nearly the whole of the 25,000 wells in America put together. The oil shot up to a height of from 200 to 300 feet, in a stream 18 inches thick, tearing away the buildings about it, and producing a roar that could be heard for several miles around. By and by a lake of oil was produced which ruined everything in its neighborhood and bankrupted its owners. The well flowed at the rate of 25,000 barrels per day for five months before it was possible to successfully cap and control it.

In 1887 another well, yielding oil at a depth of 790 feet, poured out a stream 12 inches in diameter to a height of 200 feet for 69 days. In this time it yielded 3,000,000 barrels of oil, of which one-third, at least, was lost, owing to lack of tank capacity. So much sand was thrown up that one-story buildings fifteen feet high, within 100 yards of the well, were buried out of sight, and an area of ten acres around the well was covered with sand to a depth of from one to fifteen feet. Later no oil at all could be obtained from the well.

Ordinarily wells do not continue to yield, but one well called the Kormilitza gave nearly 800 barrels per day for twelve years.

Russian methods of handling oil. In the Apsheron Peninsula the method of obtaining oil is somewhat different from that prevailing in the United States. The soil being very soft, the boring is usually accomplished by rods or tubes, rather than by ropes. Often the first tube is two feet in diameter, smaller tubes being used as the operation advances.

The wells in the Baku field which do not flow cannot be pumped in the ordinary manner, because of the large amount of sand in the oil (sometimes as great as 30 or 40 per cent.) Generally the oil is raised to the surface in cylindrical buckets holding about a barrel each.

In Russia the oil is allowed to flow into reservoirs of earth, where the sand may deposit ; later the oil is pumped to the refineries.

The Russian petroleum is distributed on three lines :

1. On the Caspian to Astrakhan and thence to the Volga River and the interior of Russia.

2. On the Caspian to ports opposite Baku, and thence to Central Asia.

3. To Batoum, and thence to western Russia and to the European points.

The various companies working the oil wells conduct the refineries, and they own lines of transportation in bulk by sea, and in tank cars by land. They also have large shops for making cars and repairing them. They maintain also large numbers of cisterns for storage of the various products on the shore.

The pipe lines at Baku are of wrought iron, cast iron offering too much resistance to the flow of the oil, especially in the winter.

In the burning of residuum from Russian petroleum in locomotives and steamers, a method similar to that used in the United States is followed. The oil is broken into minute globules by means of a blast of steam. In this form it burns easily under the boilers. Its efficiency is about double that of an equal weight of coal, not speaking of the saving in labor for stoking, removing ash, etc.

Toward the close of the year 1893 the majority of the oil producers of the Aspheron peninsula formed a union for the purpose of dealing with the sale of kerosene oil in foreign markets. The union is intended to continue operations until April, 1899. The general plan is that each member of the union shall deliver to the executive committee a determinate quantity of kerosene oil of standard quality, and then the committee shall have full power to distribute the oil in foreign countries and make final settlements with the producers.

Comparison of the quality of Baku crude oil with American. Below are presented a few of Mendeléeff's views on the subject ; apparently they are rather too favorable to the Russian oil :

1. The American petroleums, speaking generally, consist principally of true paraffins, with an admixture of olefines and traces of the benzenes.

The Baku oils on the other hand are to a large extent made up of olefines with some benzenes, paraffins, and acetylenes. They contain little or no solid paraffins. Such differences in chemical constitution might be expected to exert a marked influence on the quantity and quality of the refined products.

2. The crude Baku oils have less of the volatile components, like gasolene, than American oils.

3. The Baku oil may yield a larger proportion of burning oil than does American. (Baku about 40–50 per cent. by weight from crude.)

4. Baku oil is said to yield more and better lubricating oil than American does.

5. Baku crude oil can be distilled without leaving carbonaceous residue. But this is not by any means fully accomplished in practice. As a matter of fact the Baku oil is so distilled as to yield only about 30 per cent. of distillation products ; the balance goes into "astatki" or so-called "refuse," which is used merely as fuel.

Canada. Petroleum has been found in Quebec, Nova Scotia, and New Brunswick. In the latter territory there appears to be an immense unexplored oil region.

The chief output of oil has been from the township of Enniskillen, in the county of Lambton, Ontario. The first flowing well was struck in February, 1862, and before October of the same year there were no less than 35 wells.

Burma. In Burma there are at least 600 wells, but the richer wells show signs of exhaustion, notwithstanding the fact that some of the better ones have increased in production. Burma has yielded oil in increasing quantities from the beginning of the century until 1873. Since then the amount obtained has fluctuated. Possibly by the help of English capital, further development may take place.

East Indies. The island of Sumatra is said to contain a territory available for the obtaining of petroleum of far greater extent than that of Russia. The amount of product is at present moderate.

Galicia. In Galicia there were in the year 1891, 199 establishments engaged in the production of petroleum. (There were also 79 ozokerite mines.)

Roumania. In Roumania little oil has been obtained, but that little is of excellent quality. The reason for the imperfect development of the business is referable partly at least to the strict laws prevalent with respect to mining.

Peru. The petroleum beds of Peru are of vast extent. Already a moderate amount of oil has been produced, and efforts have been made to extend the work by the assistance of European capital.

Argentine. In the Argentine Republic comparatively little has been done, though the field seems to be ample. The oil produced has a local sale, for example, it is used on locomotives in some parts of the State.

Equador. In Equador oil is known to exist, but it has been but little worked.

Petroleum as fuel. Petroleum appears to be one of the best forms of fuel, being concentrated and portable.

1 pound of refined petroleum may evaporate 12.2 pounds of water.

1 pound of crude petroleum may evaporate 15 pounds of water.

1 pound of poor steam coal may evaporate 6.5 pounds of water.

1 pound of Pittsburg coal may evaporate 7.2 pounds of water.

In Russia petroleum is used for locomotives as well as for steamers.

Although in certain places petroleum is a more costly fuel than coal, a certain increase in the cost of coal would be likely to alter these relations.

As to use of fuel in the future, it appears likely that for the best results, fuel should be changed into gas, before consumption, in order that its store of heat energy may be developed most economically. Petroleum has the advantage of lending itself most easily and completely to this treatment.

The increased use of crude petroleum for fuel is noticeable when it is stated that of about 35,000,000 barrels produced in the United States in 1889, over 12,000,000 barrels were used for fuel, generally in place of coal.

Theories of the origin of petroleum. No theory of the origin of petroleum has yet gained general acceptance.

First theory : It is believed by some that petroleum was produced in the earth by a kind of distillation process from the remains of marine or other *plants.* If this process had indeed been carried on, it would be expected that along with the petroleum would be found materials resembling charcoal or coke. But these are not so observed.

Again, in accordance with this theory, it would be expected that petroleum would be closely associated with coal pits, but such association seldom occurs.

Second theory : Many scientists believe that petroleum has been formed from *animal deposits.* In accordance with this theory, large collections of animal matters, for example, remains of mollusks and fishes, have undergone decomposition by reason of heat and pressure. Whatever difficulties may be found in this theory, it must be admitted that in many parts of the globe, immense phosphoric deposits occur which are plainly referable to the bones of animals. Further, immense limestone deposits underlie the petroleum sands. Again, recent experiments have shown that certain animal fats, such as fish oils, when heated in closed vessels under high pressure, yield large quantities of hydrocarbons corresponding to those found in petroleum. This shows that the transformation referred to is not an impossible one.

Third theory: Some scientists have proposed the idea that petroleum has been formed and perhaps is now in process of formation from *inorganic* materials. Thus Sokoloff suggests that during the creation of this planet, the hydrocarbons formed in the period of original atomic union gathered gradually so as to produce the petroleum deposits.

Fourth theory: The Russian chemist, Mendeléeff, believes that petroleum is formed by the *action of water* at high temperatures and pressures on carbide of iron existing in the earth's crust. In this view, the fissures caused by the upheaval of mountain chains permit water to reach heated carbide of iron. Thereupon the iron combines with the oxygen of the water, producing iron ores; and the carbon combines with the hydrogen of the water, producing the hydrocarbons of petroleum. After their formation, these hydrocarbons pass up as vapor until they reach sedimentary strata cool enough to condense them. The occurrence of petroleum in active volcanic areas, as in Sicily and Japan, seems to accord with this theory. The theory receives support also from the fact that petroleum is usually found in the vicinity of mountains. An attractive feature of this hypothesis is that it assumes that petroleum is still forming beneath the surface of the earth and that the supply may be therefore looked upon as in a sense inexhaustible. Ingenious as this theory is, it is subject to many objections.

Some scientists have endeavored to make a combination of theories, with the notion that different petroleum deposits may have been produced differently, some by one chemical process, some by another.

Natural Gas.

This substance is obtained notably in Pittsburg and its neighborhood, when borings to depths varying from 500 to 2,000 feet strike the pockets containing it. At first it issues at a pressure estimated at about 1,000 lbs. per square inch—but this rapidly diminishes. (The neighborhood of Pittsburg has above 100 wells.)

The average composition of natural gas is:

Marsh gas, CH_4,	.	.	.	60. to 80.	per cent. by volume.
Hydrogen,	.	.	.	5. " 20.	
Nitrogen, .	.	.	.	1. " 12.	
Ethane, C_2H_6, .	.	.	.	1. " 8.	
Ethylene, C_2H_4,	.	.	.	0. " 2.	
Carbon dioxide, CO_2,	.	.	3. " 2.	
Carbon monoxide, CO,	.	.	trace " trace.	
Oxygen, .	.	.	.	trace " trace.	

The use of natural gas as a fuel has attained large proportions in the neighborhood of Pittsburg. It has replaced millions of tons of coal.

Asphaltum.

Asphaltum, albertite, maltha, are names applied to semi-solid bituminous substances found in the earth. They vary very much in composition and purity. In general, they are mixtures of hydrocarbons, apparently of the fatty series. They are largely used mixed with sand, limestone, or other mineral matters, for street pavements. Certain kinds of asphaltum are very valuable for waterproofing and electrical insulating purposes.

Ozocerite, or Ozokerite.

This is a natural mineral wax, somewhat similar to paraffin, but composed of C_nH_{2n}. It has of late been found to some extent in Utah. Previously, practically its only source was Galicia, in Austria. With a moderate amount of refining, it becomes white. It is a valuable substitute for beeswax. It has been considerably used for electrical insulating purposes.

CHAPTER IX.

HALOGEN DERIVATIVES OF FATTY HYDRO-CARBONS.

These are compounds produced by substituting one or more atoms of fluorine, chlorine, bromine, or iodine, alone or in combination, for hydrogen atoms in hydrocarbons. Hundreds of such compounds are known and have been studied. But only a few have obtained industrial importance.

The following table gives a few of such compounds to suggest the kind of displacements possible :

Synopsis of Methane Derivatives.

Methane, marsh gas, CH_4.

Halogen substitution compounds :

CH_3Cl	CH_3Br	CH_3I
Methyl chloride	— bromide	— iodide
CH_2Cl_2	CH_2Br_3	CH_2I_2
Methylene chloride	— bromide	— iodide
$CHCl_3$	$CHBr_2$	CHI_3
Chloroform	Bromoform	Iodoform
CCl_4	CBr_4	CI_4
Carbon tetrachloride	— tetrabromide	— tetraiodide

The following compounds of this class are worthy of special mention here :

Methyl chloride, CH_3Cl. This substance is a colorless gas which easily condenses to the liquid form and easily volatilizes again. It is prepared to a considerable extent for use in the arts. In the manufacture of aniline colors, it is employed as a means of introducing methyl into compounds in which it is desired.

It is also employed in the production of artificial cold.

Chloroform, CHCl$_3$. This substance is important when considered both from the theoretical and from the practical side. It may be produced by the action of chlorine gas on marsh gas.

It is not easily produced at present from methyl alcohol.

It is ordinarily manufactured by the action of bleaching powder upon ethyl alcohol.

Chloroform is largely used in surgery and medicine for producing insensibility to pain. While it is of untold value for such purposes, it must not be forgotten that death has often ensued from an overdose. Ethel ether, commonly called sulphuric ether, is considered a safer anæsthetic.

Iodoform, CHI$_3$, and *bromoform*, CHBr$_3$, correspond in structure with chloroform. The former is largely used in surgery.

CHAPTER X.

ALCOHOLS.

Of the Fatty Series.

The word alcohol was originally applied to the principal substance generated by the fermentation of grape juice, viz., that substance now known as ethyl alcohol, $C_2H_5 \cdot OH$. The word has since been extended so as to include a class of substances. All members of this group contain one or more molecules of the radicle hydroxyl, OH.

Alcohols are classified in two ways:

First. By the number of hydroxyl groups (OH).

A *monohydric* alcohol has one hydroxyl group.

<p style="text-align:center">*Example:* Ethyl alcohol, C_2H_5OH</p>

A *dihydric* alcohol has two hydroxyl groups.

<p style="text-align:center">*Example:* Ethylene alcohol, $C_2H_4(OH)_2$</p>

A *trihydric* alcohol has three hydroxyl groups.

<p style="text-align:center">*Example:* Propenyl alcohol, $C_3H_5(OH)_3$, (glycerol or glycerine)</p>
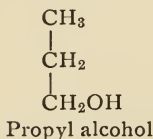
A monohydric alcohol	A dihydric alcohol	A trihydric alcohol
CH_3	CH_3	CH_2OH
$\mid$	$\mid$	$\mid$
CH_2	$CHOH$	$CHOH$
$\mid$	$\mid$	$\mid$
CH_2OH	CH_2OH	CH_2OH
Propyl alcohol	Propylene alcohol	Propenyl alcohol
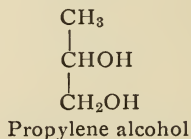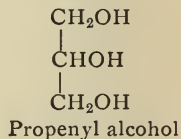
Second. By the position of the hydroxyl group.

A *primary* alcohol contains the group CH_2OH. It has the hydroxyl group attached to an atom of carbon which is attached to not more than one other carbon atom.

Examples: Primary butyl alcohol, $CH_3 \cdot CH_2CH \cdot CH_2 \cdot OH$

<p style="text-align:center">Primary isobutyl alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}$: $CH \cdot CH_2OH$</p>

<p style="text-align:center">(64)</p>

In a primary alcohol the hydrogen in a methyl residue, CH_3, is replaced by hydroxyl.

Primary alcohols, when oxidized, yield progressively aldehydes and organic acids containing respectively the original number of carbon atoms. Thus, ethyl alcohol, C_2H_5OH, by oxidation, forms first, aldehyde, C_2H_4O, or $CH_3 \cdot COH$, and then, by further oxidation, acetic acid, $C_2H_4O_2$, or CH_3COOH.

A *secondary* alcohol contains the group $CHOH$. It has the hydroxyl group attached to an atom of carbon which is attached to two other carbon atoms.

Example: Secondary butyl alcohol, $CH_3 \cdot CH_2 \cdot CHOH \cdot CH_3$

In a secondary alcohol the hydrogen in a methylene residue, CH_2, is replaced by hydroxyl.

Secondary alcohols, when oxidized, yield progressively ketones containing the original number of carbon atoms, and then organic acids containing a smaller number of carbon atoms. Thus, secondary propyl alcohol, C_3H_7OH, or $CH_3 \cdot CHOH \cdot CH_3$, by oxidation, forms first, a ketone called dimethyl ketone or acetone, C_3H_6O, or $CH_3 \cdot CO \cdot CH_3$; and then, by further oxidation, more than one acid having fewer carbon atoms.

A *tertiary* alcohol contains the group COH. It has the hydroxyl group attached to an atom of carbon which is attached to three other carbon atoms.

Example: Tertiary isobutyl alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}$: $COH \cdot CH_3$

In a tertiary alcohol the hydrogen in a methenyl residue, CH, is replaced by hydroxyl.

Tertiary alcohols, when oxidized, do not yield aldehydes nor ketones nor *corresponding* acids. They yield, however, two non-corresponding acids having an amount of carbon lower than that of the original alcohol. The lowest alcohol of this class is tertiary butyl alcohol, C_4H_9OH, or $(CH_3)_3COH$.

Butane, C_4H_{10}, is the lowest paraffin compound forming all three : primary, secondary, and tertiary alcohols. They all have the empirical formula, $C_4H_{10}O$.

I. Alcohols with One Atom of Oxygen.

These constitute an important group. A large number of members are known. Commercially the most important are methyl alcohol and ethyl alcohol.

The following list refers to about eighty monohydric alcohols now known ; only a few are expressed in detail.

It will be seen that those having the smaller number of atoms are inclined to be liquid at ordinary temperature ; as the numbers of atoms in the molecule increase, the tendency toward solidity

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increases. The comparatively regular advances in boiling points and melting points are very significant. *They represent a fundamental tendency* which pervades the field of organic chemistry.

Fatty Alcohols--Monohydric.

		Boiling or melting point, Degrees C.		Empirical formula.	
1.	Methyl alcohol,	boils,	67.	$C H_4 O$	$CH_3 \cdot OH$
2.	Ethyl "	"	78.4	$C_2 H_6 O$	$CH_3 \cdot CH_2 OH$
3.	Propyl "	"	97.4	$C_3 H_8 O$	$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$
					$CH_3 \cdot CH(OH) \cdot CH_3$
4.	Butyl "	"	117.	$C_4 H_{10} O$	$CH_3 \cdot (CH_2)_2 \cdot CH_2 \cdot OH$
					$CH_3 \cdot CH(OH \cdot CH_2 \cdot CH_3$
					$(CH_3)_2 \cdot CH \cdot CH_2 \cdot OH$
					$(CH_3)_2 \cdot C(OH) \cdot CH_3$
5.	Amyl "	"	137.	$C_5 H_{12} O$	eight forms known.
6.	Hexyl "	"	157.	$C_6 H_{14} O$	fourteen " "
7.	Heptyl "	"	175.5	$C_7 H_{16} O$	thirteen " "
8.	Octyl "	"	195.5	$C_8 H_{18} O$	nine " "
9.	Nonyl "	melts, —5.		$C_9 H_{20} O$	six " "
10.	Dekyl "	"	7.	$C_{10} H_{22} O$	five " "
11.	Hendekatyl "			$C_{11} H_{24} O$	two " "
12.	Dodekyl "	"	24.	$C_{12} H_{26} O$	two " "
13.	Dihexyl carbinol,	"	42.	$C_{13} H_{28} O$	one form "
14.	Tetradekyl alcohol,			$C_{14} H_{30} O$	two forms "
15.	Cetyl "	"	49.	$C_{16} H_{34} O$	one form "
16.	Oktadekyl "	"	59.	$C_{18} H_{36} O$	one " "
17.	Medicagol,	"	80.	$C_{20} H_{42} O$	one " "
18.	Dilauryl alcohol,	"	75.	$C_{23} H_{48} O$	one " "
19.	(A primary alcohol),			$C_{25} H_{52} O$	one " "
20.	Ceryl alcohol,	"	79.	$C_{27} H_{58} O$	three forms "
21.	Myricyl "	"	85.	$C_{30} H_{62} O$	one form "
22.	Dipalmityl carbinol,	"	85.	$C_{31} H_{64} O$	one " "
23.	Tarchonyl alcohol,	"	82.	$C_{50} H_{102} O$	(?) one " "

Methyl alcohol, commonly called wood spirit, $CH_3 OH$. This substance is a colorless volatile liquid resembling in some ways ordinary or ethyl alcohol. It strictly resembles the latter in its plan of molecular structure.

Methyl alcohol is ordinarily produced by the destructive distillation of wood. Wood is placed in a retort, usually of iron. Upon heat being applied to the retort, the wood undergoes decomposition. Vapors of various kinds are driven off, and when they are condensed in the receiver provided, they are found to contain a great many different substances. Among them are water, methyl alcohol, acetic acid, tarry matters. This impure mass may be redistilled with sodium hydroxide, whereupon a purer methyl alcohol is obtained.

Methyl alcohol and certain other methyl compounds are now produced as a by-product by proper treatment of certain residues of the beet-sugar industry. The materials known as vinasses were formerly thrown away. They are now, however, subjected to a destructive distillation whereby methyl compounds are produced in the distillate and certain potassium salts are obtained in the dry residue.

Methyl alcohol is used to some extent as a substitute for ethyl alcohol. In most commercial nations there prevails the policy of securing a large revenue by a tax upon articles considered injurious. With this principle in view, liquids containing ethyl alcohol are heavily taxed. The tax, however, bears not only upon that alcohol which is intended to be or may be used for drinking purposes, but also upon such as is used as a solvent for gums or resins in the arts. In order to relieve manufacturers from this impost, the English government liberates from taxation what is called methylated spirit; that is, mixtures of 90 per cent. ethyl alcohol and 10 per cent. methyl alcohol. This regulation is based upon the theory that the methylated spirit cannot be used for drinking on account of the offensive flavor imparted by the methyl alcohol, but that the latter does not unduly reduce the solvent power of the ethyl alcohol.

Synopsis of Inorganic Synthesis of Methyl Alcohol.

1. Produce marsh gas, CH_4. Submit sulphuretted hydrogen to the action of carbon disulphide in presence of copper.

2. Produce methyl chloride, CH_3Cl. Submit marsh gas to chlorine gas in diffused sunlight.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
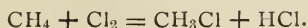
3. Produce methyl alcohol. Submit methyl chloride to the action of potassium hydroxide.

$$CH_3Cl + KOH = CH_3OH + KCl.$$

Ethyl alcohol, C_2H_5OH. Ethyl alcohol is looked upon as corresponding to substances like potassium hydroxide, KOH.

The substance was recognized in the very ancient times as formed in certain processes of fermentation, particularly the fermentation of wine. Many different kinds of fermentation have been recognized ; this particular kind has, therefore, been specially designated as the vinous fermentation. The juice of the grape, like that of many other fruits, contains a variety of substances. Among them may be mentioned sugar, water, and certain albuminous matters. Such liquids often set up fermentation —apparently, though not really, of themselves. Sometimes the operation is initiated or else hastened by the addition of yeast. The fermentation, once started, proceeds for a considerable time. The principal change is now known to be due to the sugar present, the amount of alcohol formed depending strictly on the amount of sugar that undergoes metamorphosis. Further, it is noted that the metamorphosis is strictly dependent upon the presence of minute organisms in the juice. These organisms, called ferments, are vegetable in nature. If by any means, all the organisms in a portion of fruit juice are destroyed, fermentation does not proceed until others have been introduced either from the air or in what is called yeast. It is worthy of note, also, that the albuminous matters favor the process. They seem to act as a sort of pabulum for the microscopic plant which carries on fermentation. When fermentation has proceeded to a certain extent, the alcoholic product stops the process by somehow interfering with the vital processes of the microscopic plant.

Under certain circumstances, fruit juices like wine and cider are capable of a further fermentation called souring, or the acetous fermentation ; in such case that alcohol produced in the vinous fermentation is changed into acetic acid.

In the change from sugar to alcohol, carbon dioxide is evolved. This manifests itself in the froth of malt liquors like ale, and in the gas that escapes from certain sparkling wines like champagne.

But ethyl alcohol and carbon dioxide are by no means the only substances produced during vinous fermentation. Certain organic acids and organic ethers are formed, their character and amount depending on the nature of the original fruit from which the sugary juice was obtained. These ethers impart flavor to the beverage formed. They do the same in the case of distilled spirits afterwards manufactured from the fermented wine.

For the preparation of ethyl alcohol, then, ordinarily some sugary substance is fermented. The next important step is distillation. The fermented liquor, being introduced into a suitable retort, commonly called a still, is heated ; the operation being performed with the greatest care. From the liquor the alcohol is expelled as vapor ; as such it passes over into the condenser, and there returns to the liquid state. Some water vapor goes over with it, and some alcohol remains in the still ; for water and alcohol have so great an affinity for each other that it is almost impossible to separate them perfectly.

The ordinary strong alcohol of commerce is called ninety-five per cent. alcohol ; that is, it contains in the neighborhood of five per cent. of water. In some cases, the water may be largely—but not entirely—removed by distilling the ninety-five per cent. alcohol with quicklime or potassium carbonate, or some other substance having a strong affinity for water. The alcohol vapor when condensed in a suitable receiver affords what is called absolute alcohol.

For some purposes, in the arts, weaker alcohol may be used. That called proof spirit contains about fifty per cent. by weight of alcohol. Reference has already been made (see page 67) to methylated spirit, a mixture of ninety per cent. ethyl alcohol and ten per cent. methyl alcohol.

The ordinary method for producing alcohol has been detailed. There are many other methods of obtaining the substance by the proper reaction of ethyl compounds. These latter, however, have a theoretical interest rather than a practical one. One process is given below. Stated in full, it shows how, by organic synthesis, ethyl alcohol may be produced from the lifeless elements composing it without the intervention of the processes of living animals or plants.

Inorganic Synthesis of Ethyl Alcohol.

1. Prepare acetylene, C_2H_2, by running the electric current from carbon poles through an atmosphere of hydrogen.

$$C_2 + H_2 = C_2H_2$$
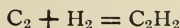
2. Prepare ethylene, C_2H_4, by uniting acetylene with hydrogen by the aid of platinum black.

$$C_2H_2 + H_2 = C_2H_4$$
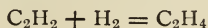
3. Prepare hydrogen ethyl sulphate, $HC_2H_5SO_4$, by passing ethylene through concentrated sulphuric acid.

$$C_2H_4 + H_2SO_4 = HC_2H_5SO_4$$

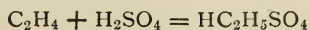4. Prepare ethyl alcohol by heating ethyl sulphuric acid with potassium hydroxide.

$$HC_2H_5SO_4 + 2KOH = C_2H_5OH + H_2O + K_2SO_4$$

Uses of ethyl alcohol. The enormous consumption of alcoholic beverages, as shown by statistics, cannot escape observation. While ethyl alcohol is considered by physicians as a most valuable stimulant when properly used, the results of the improper use of alcoholic liquids are, as every one must see, most lamentable.

Alcohol has a large number of important uses in science and in the arts. Enormous quanties are used in museums for the preservation of natural history specimens.

In the chemical laboratory large quantities are used in *inorganic work* as a special solvent, in *organic work* both as a solvent and as a source of the radicle ethyl to be transferred or transformed into other compounds. It is certainly one of the main reagents of the organic laboratory.

Alcohol is used in a variety of arts.

Thus it is used as a *fuel* by jewelers in blowpipe lamps, as a *solvent* in the preparation of transparent soap, in the securing of alkaloids, etc., from vegetable products, in the blending of essential oils in perfumery, in the preparation of gums and resins for varnish and enamel, and for the stiffening of felt hats, also in the preparation of collodion, as a *special source of ethyl* in the manufacture of artificial fruit extracts and flavoring compounds, and in the preparation of fulminates for use in ammunition.

Alcoholic Liquors.

Alcoholic liquors are usually divided into three groups : malt liquors, wines, and spirits.

In the preparation of *beer and similar malt liquors*, barley is the grain chiefly used.

1. The first step is the germination of the grain or sprouting. By this process the starch is altered into dextrin and glucose. When the sprouting has advanced sufficiently it is checked by heating and drying in a "kiln." The barley has now become "malt."

2. The malt is ground and then subjected to the "mashing" process. In this the malt is treated with water warmed to a proper temperature. The change of starchy matters to saccha-

rine matters is advanced and soluble substances are dissolved. A liquor called "wort" is obtained.

3. The wort is drawn off, hops are added, and the liquid is boiled; later it is drawn off again and carefully cooled.

4. Next yeast is added. The sugars split up into alcohol and carbon dioxide, The latter as it rises makes the liquid foamy.

5. The liquor is "racked off" so as to separate the clear part from any matter that would make the beer turbid.

The amount of alcohol in the finished beer varies from three to eight per cent. In some cases, beer is subjected to a process called *pasteurization*. This process consists in raising the beer to such a temperature that the microscopic plants that favor fermentation are destroyed. If this sort of sterilization were not performed, the vinous fermentation might be followed by an acetous fermentation; in other words, the beer might turn sour.

In the production of *wines*, grapes are commonly used. They are often selected with great care. Sometimes they are separated from the stems and sometimes not.

1. The grapes are pressed, care being taken not to crush the seeds or the twigs. The juice produced is called "must," the solid residue is called "marc" or "pomace." The must contains grape sugar as its most important constituent. Many other substances have been recognized, among which the following ought to be noted: tartaric, tannic, malic, and other acids, albuminoids, coloring matters, mineral matters, notably potassium and calcium compounds.

2. The must is fermented. This process will commence of itself by reason of microbes in the air or on the grapes used. Sometimes carefully selected yeast is used (the kind of yeast is of the highest importance). Fermentation proceeds slowly, often for months. During fermentation the sugar changes to alcohol and carbon dioxide; the production of the former often determines the separation of a sediment called "wine lees" or "argol," an impure potassio-calcium tartrate (a crude tartar, of considerable importance as a source of cream of tartar and tartaric acid.)

3. Other operations of great variety are carried on. They are intended to alter the character or raise the quality of the wine produced.

Sometimes wine is pasteurized; in other cases, the liquid being bottled or otherwise enclosed, the fermentation stops by reason of the considerable accumulation of alcohol which suppresses the action of the ferment that formed it. Wines contain normally from seven to seventeen per cent. of alcohol. In some cases, however, the amount is artificially increased by adding previously distilled spirits.

Spirits, such as whiskey, brandy, rum, are manufactured by first conducting the fermentation process and afterward the distillation process. The fermentation process is practically similar to that detailed. In the distillation process, the fermented liquor is distilled and a strong alcohol is produced. The distilled liquid may contain from forty to fifty per cent. of alcohol, the remainder being water — except that certain etherial compounds are present which give to the spirit its peculiar flavor.

Thus, whiskey contains certain compounds derived from the fermentation of the grain from which it is produced. Brandy, being distilled from wines, contains flavoring compounds derived from the grape, while rum, which is distilled from molasses, has a still different set of flavoring compounds referable to its origin.

II. Alcohols with Two Atoms of Oxygen (Glycols.)

Many members of this group are known. They may be derived from one or more radicles of one or more of the hydrocarbon series already mentioned.

The first member of the group is itself called glycol. It is ethylene glycol, $C_2H_4(OH)_2$, or $CH_2OH \cdot CH_2 \cdot OH$.

III. Alcohols with Three Atoms of Oxygen.

Many members of this group are known. The most important is glycerine, now called glycerol.

Glycerin, now called glycerol, (*propenyl alcohol*), $C_3H_8O_3$, or $H_2COH \cdot CHOH \cdot CH_2OH$. This is a well-known colorless liquid of syrupy consistency. It has a sweetish taste. It mixes readily with alcohol or water. Indeed, when exposed to ordinary air, it absorbs moisture. When pure it may be distilled without decomposition. It distils better, however, in contact with a current of steam.

Glycerol is produced in some processes of fermentation ; for example, during the vinous fermentation of sugar.

Glycerol is ordinarily manufactured from lard, but it may be produced from other true fats.

Glycerin was recognized by Scheele as early as 1779. Chemical knowledge on this subject has been very much enlarged since by the studies of Chevreul, Berthelot, and others, on fats, and since modern manufacturing operations have produced large quantities of glycerin in response to modern demands. There are two general methods of producing this substance :

First, by the process of saponification. In making soap, dry fats, (that is, glycerides) are boiled with a strong alkali. This substance combines with the fat acids, forming soap, and at the same time liberates glycerin. The soap may be separated from the mixture, and so may the glycerin.

If, instead of potassium hydroxide or sodium hydroxide, lead oxide, called litharge, PbO, is boiled with the glyceride, the latter gives rise to the same reaction, only the salt produced is called lead soap. It may be classed according to circumstances as stearate, palmitate, or oleate of lead, or a mixture of these salts. The lead soap, however, different from soaps of the alkalies, is insoluble in water. Thus, it is more easily separated from the mixture, and it gives more favorable opportunity for subsequent separation of the glycerin.

Second, natural fats may be dissociated by the action of superheated steam. A separation is accomplished whereby the glycerin sinks to the bottom of the mixture, and the fatty acids rise. The glycerin may be drawn off subsequently, and subjected to further purification.

Glycerin has a very large number of uses in pharmacy and in other arts. Generally speaking, it is a valuable solvent. It does not solidify readily, and it does absorb moisture. On this account it is employed to keep membranes soft and pliable. It is employed for certain purposes in photography. It is said to be used very much in brewing operations in the manufacture of beer. It has been used in the so-called wet gas meters in place of water, for use during the prevalence of low temperature. Enormous quantities are employed in the manufacture of nitroglycerin for use, alone or with other substances, as an explosive.

Nitroglycerin, propenyl trinitrate, $C_3H_5(NO_3)_3$. This remarkable substance, now largely used as an explosive, seems to have

been brought to notice as a remedy for headache, under the name of glonoin oil. It was first prepared in the United States and recommended as a medical remedy. Its explosive properties were soon discovered; and at length, as other nitrates, such as cellulose nitrate or gun-cotton, came into use, nitro-glycerin was carefully studied. The great development of this explosive may be referred largely to Alfred Nobel, who introduced it for use in blasting. Of late, it has come to be very extensively employed on great public works, such as railway tunnels, where large masses of rock must be broken down. It has been employed to great advantage in driving deep petroleum wells. If a well which has attained great depth fails to afford oil, a cartridge is in some cases lowered to the bottom and then exploded by electricity; thereupon seams appear to be opened in the subterranean rock, through which oil or gas may flow. This method has been largely used in Pennsylvania, and in many cases has successfully accomplished its purpose.

It is a curious fact that nitroglycerin may be burned without any explosion. It is exploded best by some form of percussion. A cartridge of it is usually provided with a special exploder containing fulminating mercury. The fulminate, being decomposed by an electric spark, strikes a blow upon the nitroglycerin, which itself thereupon explodes with frightful force. Many terrible explosions have occurred from the decomposition of nitroglycerin by some concussion by accident or otherwise. On account of such danger, it has now become the custom where great public works demand the use of this explosive, to manufacture it upon the spot. A small house is usually constructed of light materials, and it is surrounded by a parapet of earth. Within the house the explosive is manufactured. In case of an accident, the loss of the building is not material, and the parapet serves to localize the effects.

Nitroglycerin is produced by the action of a mixture of concentrated nitric acid and concentrated sulphuric acid upon glycerin. The mass is allowed to stand for some time, free from jarring and in a cool place. By and by, nitroglycerin separates out as an oily liquid. It is drawn off into water and thoroughly washed. This washing is of the first importance, since acids remaining in the nitroglycerin are liable to determine a decomposition of the latter with violent explosion.

Nitroglycerin is rarely used alone. It is ordinarily mixed with other substances, either for convenience in transportation or otherwise to diminish the danger of handling. The commonest

preparation is that called dynamite, which consists of three parts of nitroglycerin absorbed in one part of *infusorial* earth. This infusorial earth is a mass of silicious skeletons of microscopic vegetables. It is very porous and serves to hold the nitro-gylcerin in the form of a paste. This paste may then be placed in paper wrappers so as to form suitable cartridges. A cartridge of dynamite may be subjected to a more severe blow than an equivalent mass of nitroglycerin, for the dynamite represents a sort of paste which may yield to the blow and change its shape rather than to suffer contraction as the nitroglycerin alone seems to.

Many frightful accidents have occurred from the careless use of nitroglycerine or its preparations. If the subject is carefully considered, it is discovered that many of these accidents are largely due to gross carelessness. Thus, in some cases, a frozen mass of nitroglycerin has been placed by a workman upon a hot stove to melt. Again, the use of this powerful explosive in quarrying and similar blasting operations has extended enormously; while the accidents appear not to have increased in like proportion. Thus it appears that in the vast majority of cases it is used with entire safety.

Alcohols with Four, Five, Six, Seven, Eight, Atoms of Oxygen.

To the *six set* belong mannite and dulcite, isomers, white solids sweet in taste, derived from a vegetable substance called manna :

Mannite, $C_6H_{14}O_6$, $CH_2OH(CHOH)_4CH_2OH$
Dulcite, $C_6H_{14}O_6$, $CH_2OH \cdot C(OH)_2 \cdot CH_2(CHOH)_2CH_2OH$
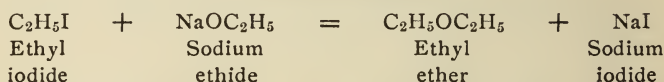
CHAPTER XI.

ETHERS, SIMPLE AND MIXED.

Esters, Etc.

The word ether was originally applied to what is now known as ethyl ether; it now applies to a class of organic bodies having the general formula R—O—R, in which R designates an alkyl radicle like ethyl, C_2H_5. If the two alkyls are alike, the ether is called *simple;* if they are different, the ether is called *mixed.*

The ethers correspond in general to the inorganic metallic oxides, for example: potassium oxide, K_2O, or K—O—K.

There are two important general methods for the preparation of ethers:

1. By action of alkyl iodides on sodium alcohols:

$$C_2H_5I \quad + \quad NaOC_2H_5 \quad = \quad C_2H_5OC_2H_5 \quad + \quad NaI$$

Ethyl	Sodium	Ethyl	Sodium
iodide	ethide	ether	iodide

2. By action of sulphuric acid on an alcohol. (In this case the action is virtually a withdrawal of water. The operation is, in fact, more complex. It is discussed later.)

$$2C_2H_5OH \quad = \quad C_2H_5OC_2H_5 \quad + \quad H_2O$$

Ethyl	Ethyl	Water
alcohol	ether	
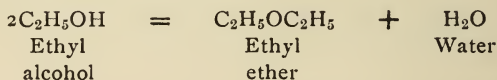
(Mixed ethers may be produced by both methods; but then the compounds used must have different alkyl radicles.)

The first fatty ether, methyl ether $(CH_3)_2O$, is a gas, at ordinary temperature. Advancing in the series, volatile liquids are found.

It is a remarkable fact that the ethers boil at lower temperatures than their alcohols.

Many ethers are known, also many substitution products and many isomers.

Dimethyl ether, $(CH_3)_2O$. This substance is worthy of mention because it corresponds strictly with ethyl ether, the latter being the anaesthetic so much employed in surgery. From the general laws of chemical philosophy, it might be expected that methyl ether would be more volatile than ethyl ether. This is indeed the case. At ordinary temperatures it is a colorless gas, but at —21°C it condenses to a colorless but very volatile liquid. Just as ethyl ether is produced by the action of sulphuric acid upon ethyl alcohol, so methyl ether is produced by the action of sulphuric acid upon methyl alcohol.

Ethyl oxide, or *ethyl ether* (commonly called sulphuric ether), $(C_2H_5)_2O$. This substance is very important, both from the theoretical and the practical side. Its power of producing insensibility to pain has led to its wide-spread employment in surgery. Certainly any process or thing that diminishes human misery must be considered as useful in the highest degree.
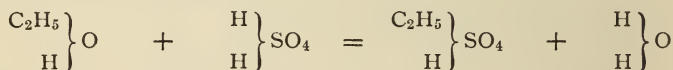
Sir Humphry Davy and others, working in what was called the Pneumatic Institution of Dr. Beddoes, made a number of experiments upon the inhalation of gaseous vapors. While these led to the discovery of the effects of nitrogen monoxide (nitrous oxide) they nearly proved fatal to Davy himself. Investigation in this line proceeded, however, and in 1818 Faraday observed some of the physiological properties of ether. The practical application of this substance seems to be referable to Dr. Long, who applied it in 1842. Dr. Morton, of Boston, is ordinarily recognized as the first to bring its use to public attention as an adjunct in surgery. His claims as to priority have been disputed by Professor Jackson, of Boston. In England, Sir James Simpson, of Edinburgh, appears to have been the pioneer in its employment. It is worthy of remark with respect to ether, that, like other useful and valuable inventions, its early progress was in the face of great opposition.

On the theoretical side, ether has been very carefully studied because of certain peculiarities incidental to its manufacture. The substance is made by heating together under proper conditions, sulphuric acid and alcohol. It was soon discovered that a given amount of sulphuric acid was capable of changing into ether a much larger quantity of alcohol than was at first supposed possible. This possibility was published by a French chemist, Cadet, in 1774. One of his competitors, Beaumé, objected to Cadet's method. The latter offered the capital reply that he was selling his product at forty sous an ounce while Beaumé was charging twelve livres. For a long time the nature of the process
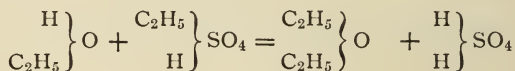
was not understood.   Eventually, however, its careful study
resulted in important contributions to chemical theory.

Ether is now manufactured by what is called the continuous process.   The
apparatus employed consists essentially of a retort, a condenser, and a receiver.
In the retort the transformation of alcohol into ether proceeds. · The ether
vapor is liquified in the condenser and collected in the receiver.   A mixture of
ethyl alcohol and sulphuric acid is introduced into the retort.   Upon heat-
ing the mixture to a proper temperature, ether is produced.   Now, upon
steadily adding more alcohol, in properly graduated quantity, the same portion
of sulphuric acid is capable of carrying on the transformation of the alcohol
continuously.

The present theory of the operation is as follows :   The change from alcohol
to ether advances through an intermediate stage.   In this stage there is pro-
duced a compound called ethyl sulphuric acid, $C_2H_5HSO_4$.   With this fact in
mind, the following explanation may be understood.   When sulphuric acid is
heated with ethyl alcohol, ethyl sulphuric acid is first produced in accordance
with the following equation :

$$\left.\begin{array}{c}C_2H_5\\H\end{array}\right\}O \quad + \quad \left.\begin{array}{c}H\\H\end{array}\right\}SO_4 \quad = \quad \left.\begin{array}{c}C_2H_5\\H\end{array}\right\}SO_4 \quad + \quad \left.\begin{array}{c}H\\H\end{array}\right\}O$$

Next, the ethyl sulphuric acid acts upon a new portion of ethyl alcohol,
whereby two most important results are attained.   First, ethyl ether, the thing
desired, is produced.   Second, sulphuric acid, the reagent desired for subse-
quent operations, is formed anew.   This second stage may be understood by a
consideration of the following equation :

$$\left.\begin{array}{c}H\\C_2H_5\end{array}\right\}O + \left.\begin{array}{c}C_2H_5\\H\end{array}\right\}SO_4 = \left.\begin{array}{c}C_2H_5\\C_2H_5\end{array}\right\}O \quad + \left.\begin{array}{c}H\\H\end{array}\right\}SO_4$$

While then, theoretically, the process is continuous because of the continu-
ous reproduction of sulphuric acid, it is found practically that certain conditions
interfere with the perfect working of the operation which make it necessary to
employ from time to time a small additional supply of material.

Ether has other uses beside those in surgery.   It is a valuable
solvent for fats.   It is used in the preparation of collodion, which
is a solution of nitrocellulose in ether.   It has been largely
employed in the artificial production of ice, although at present
ammonia gas is replacing it in this process.

Esters, or Etherial Salts.

An ester is a salt containing an alkyl radicle, or its equivalent.
Thus ethyl acetate, $C_2H_5 \cdot OOC \cdot CH_3$ is an ester ; hydrogen ethyl
sulphate, $HC_2H_5SO_4$ is an ester ; ethyl chloride, C_2H_5Cl is an
ester.

A diatomic alcohol may form more than one ester. Thus glycol, $C_2H_4(OH)_2$ may form

The basic ester, $OH \cdot C_2H_4 \cdot Cl$
The neutral ester, $Cl \cdot C_2H_4 \cdot Cl$

Esters occur in nature in fruits and flowers; these often owe their odors to one or more esters present.

There are many general methods of forming esters:

1. By direct action of an acid upon an alcohol.
2. By exchange between an alkyl iodide and a silver salt of the acid whose ester is to be formed.

The esters are generally volatile liquids, possessing agreeable odors, lighter than water, insoluble or but slightly soluble in water, soluble in alcohol.

The esters are generally easy of decomposition. Calcium oxide and barium oxide (dry) generally act on esters so as to form two kinds of compounds: in the one the metal combines with the acid radicle of the ester; in the other the metal combines with oxygen and the alkyl radicle.

The following esters are worthy of mention:

Methyl chloride, CH_3Cl, see p. 62.
Chloroform, $CHCl_3$, see p. 63.
Ethyl chloride, C_2H_5Cl, see p. 17.
Ethyl nitrite (sweet spirit of nitre), $C_2H_5NO_2$
Ethyl nitrate (nitric ether), $C_2H_5NO_3$
Ethyl sulphate, $(C_2H_5)_2SO_4$
Hydrogen ethyl sulphate, $HC_2H_5SO_4$
Propenyl trinitrate (nitroglycerin), $C_3H_5(NO_3)_3$, see p. 73.
Methyl butyrate, (pineapple oil), $CH_3 \cdot OOC \cdot C_3H_7$
Ethyl acetate (acetic ether), $C_2H_5 \cdot OOC \cdot CH_3$
Amyl acetate (pear oil), $C_5H_{11} \cdot OOC.CH_3$

Sulphur (and other) Alkyl Compounds.

The alkyl radicles are capable of forming a series of compounds corresponding to many of the oxygen organic compounds already mentioned, except that oxygen is replaced by sulphur or selenium or tellurium. The sulphur alcohols are called *mercaptans*. For example:

Ethyl alcohol, C_2H_5OH Ethanethiol, C_2H_5SH
Ethyl ether, $(C_2H_5)_2O$ Ethanethioethane, $(C_2H_5)_2S$

CHAPTER XII.

ORGANIC ACIDS.

Fatty Series.

The organic acids, like the compounds already referred to, are usually divided into two series, the fatty and the aromatic. Only the fatty will be discussed here.

It is not easy to make a comprehensive definition of the term organic acid.

The stronger organic acids have certain common properties in marked degree: (1) They have sour taste; (2) they redden blue litmus; (3) they combine with metals to form salts; (4) they neutralize alkalies, forming salts; (5) they act on metallic carbonates liberating carbon dioxide and forming salts; (6) when they form salts as described, a part of the hydrogen of the acid is replaced by metal. But some organic substances recognized as acids do not perform all of the acts described.

The organic acids contain one or more groups of the radicle hydroxyl, COOH.

Some of the organic acids exist free in animal or vegetable matters; some exist there in a state of combination; some are produced by processes of natural fermentation or decay; some are produced by distinctly artificial chemical operations.

The organic acids may be obtained by a great variety of methods, generally by mere processes of separation including liberation by other stronger acids; in many cases even the acids known in nature may be built up synthetically from lifeless elementary substances.

Each organic acid is considered to be derived by oxidation from a corresponding parent alcohol.

Some of these acids are gaseous, some are liquid, some are solid, at ordinary temperatures. Generally they are soluble in water; but some are not.

The number of fatty acids known is very great; many isomers and substituted compounds, also acids, are recognized.

(80)

Classification of the fatty acids is somewhat difficult. It is usually dependent upon the number of oxygen atoms in the molecule. Thus, starting with that acid having two atoms of oxygen, the series advances, step by step, to that having fourteen atoms; one having twenty-eight atoms of oxygen is known. Thus about sixteen groups are recognized; in many cases, however, these are divided into several subordinate classes.

Conspectus of Fatty Acids.

Acids of the series A, B, C, D, etc., contain respectively radicles of the formulas $C_n H_{2n}$, $C_n H_{2n-2}$, $C_n H_{2n-4}$, $C_n H_{2n-6}$, etc.

1st. Acids with two atoms of oxygen. (Representatives are known of all the four series of fatty hydrocarbons, A, B, C, D.) *Examples:* A. Many acids of the series commencing with formic acid.—B. Many acids of the acrylic series: oleic acid.—C and D.

2d. Acids with three atoms of oxygen. (Representatives are known of all the four series, A, B, C, D.) *Examples:* A. Carbonic, glycollic, lactic acids. —B. Ricinoleic acid.—C and D.

3d. Acids with four atoms of oxygen. (Representatives of six series, A, B, C, D, E, F.) *Examples:* A—B. Oxalic, malonic, succinic, suberic acids.— C. Fumaric and maleic acids.—D, E, F.

4th. Acids with five atoms of oxygen. (Representatives of five series, A, B, C, D, E.) *Examples:* A—B. Malic acid.—C, D, E.

5th. Acids with six atoms of oxygen. (Representatives of five series, A, B, C, D, E.) *Examples:* A—B. Tartaric acid.—C, D, E.

6th. Acids with seven atoms of oxygen. (Representatives of six series, A, B, C, D, E, F.) *Examples:* A—B—C. Citric acid.—D, E, F.

7th. Acids are known with eight, nine, ten, eleven, twelve, thirteen, fourteen, sixteen, twenty, and twenty-eight atoms of oxygen. In some of these there are several series.

The total number of fatty acids known is very great. Only a few can be mentioned.

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I. Fatty Acids Containing Two Atoms of Oxygen, $C_n H_{2n} O_2$.

$C H_2 O_2$	Formic acid
$C_2 H_4 O_2$	Acetic "
$C_3 H_6 O_2$	Propionic "
$C_4 H_8 O_2$	Butyric "
$C_5 H_{10} O_2$	Valeric "
$C_6 H_{12} O_2$	Caproic (or hexoic) acid
$C_7 H_{14} O_2$	Oenanthylic (or heptoic) acid
$C_8 H_{16} O_2$	Caprylic "
$C_9 H_{18} O_2$	Pelargonic "
$C_{10} H_{20} O_2$	Capric . "
$C_{11} H_{22} O_2$	Undekylic "
$C_{12} H_{24} O_2$	Lauric "
$C_{13} H_{26} O_2$	Tridekylic "
$C_{14} H_{28} O_2$	Myristic "
$C_{15} H_{30} O_2$	Isocetic "
$C_{16} H_{32} O_2$	Palmitic "
$C_{17} H_{34} O_2$	Margaric "
$C_{18} H_{36} O_2$	Stearic "
$C_{19} H_{38} O_2$	Nondekylic "
$C_{20} H_{40} O_2$	Arachidic "
$C_{22} H_{44} O_2$	Behenic "
$C_{24} H_{48} O_2$	(not named)
$C_{25} H_{50} O_2$	Hyaenic "
$C_{27} H_{54} O_2$	Cerotic "
$C_{30} H_{60} O_2$	Melissic "
$C_{34} H_{68} O_2$	Dicetylacetic "

Formic acid, $HOOC \cdot H$.   This acid occurs in the bodies of certain red ants ; also in certain stinging nettles.   It was noticed as early as 1670, when from red ants an acid substance was produced which was then recognized as in some sense corresponding to acetic acid.

Formic acid may be looked upon as methyl alcohol in which one atom of oxygen has replaced two atoms of hydrogen.   Thus :

Methyl alcohol	CH_3OH
Formic acid	$CHOOH$

Formic acid is ordinarily prepared by a destructive distillation of oxalic acid.   The oxalic acid mixed with glycerine is heated in

a flask provided with an evolution tube, the tube being dipped into a suitable receiver; by the hot bath of glycerine the oxalic acid is decomposed, with the production of formic acid and other substances. The formic acid may be collected in the receiver as a colorless liquid. Formic acid is a liquid that has a peculiar and painful effect upon the skin. It acts upon metallic oxides forming a large number of perfectly definite formates. Cupric formate, a blue salt, soluble in water, is an example.

Acetic acid, $HOOC \cdot CH_3$. The ancients were well acquainted with acetic acid in its crude form in vinegar. They knew that when the fermentation of wine proceeds to a certain degree, a sour substance is produced. Moreover, they used the substance as a sort of chemical solvent in addition to its employment as a condiment.

"The ancients held exaggerated views respecting the solvent power possessed by vinegar. This is shown by the well known story related by both Livy and Plutarch, of Hannibal dissolving the Alps by means of vinegar; whilst Vitruvius states that silicious rocks which can be attacked neither by the chisel nor by fire, are dissolved when heated and then moistened with vinegar."

There are four general methods employed in the preparation of acetic acid : (1) by the acetous fermentation of ethyl alcohol ; (2) by chemical oxidation of ethyl alcohol ; (3) by the dry distillation of carbohydrates, such as wood and other organic substances ; (4) by liberation from its salts, the acetates.

(1) When sugar undergoes the vinous fermentation into ethyl alcohol in the preparation of wine, beer, and similar liquids, there is always a tendency toward a further fermentation called *the acetous*, whereby the ethyl alcohol changes into acetic acid. The acetous fermentation proceeds under the influence of the growth of a peculiar microbe called *mycoderma aceti;* but the process is essentially an oxidizing one, and access of air is necessary. In the commercial production of acetic acid, large casks are provided. They are partly filled with shavings of wood. Upon the wood a certain portion of vinegar is poured. This vinegar contains, already, microbes capable of carrying on acetous fermentation. In due time, alcohol or some alcoholic liquid is added. Fermentation soon sets up whereby the alcohol is turned into acetic acid, air being furnished through perforations provided at certain suitable points in the cask.

The process, which was formerly an empirical one, has been carefully studied, so that now it is placed upon a thoroughly scientific basis. It is recognized that the temperature should be maintained neither too high nor too low; if too

high, alcohol is lost by evaporation; if too low, fermentation does not proceed with sufficient rapidity. It is well known that a graduated supply of air is requisite, and this is carefully provided. Further, the proper kind of microbes must be present.

(2) In the chemical oxidation of alcohol, this substance changes first into aldehyde, C_2H_4O; and then into acetic acid, CH_3COOH. This process may be employed to demonstrate the chemical formation of acetic acid, but it has not yet been successful as an industrial operation. In order to conduct it a series of shelves supporting shallow dishes of alcohol and small masses of *platinum black*, are provided, and the whole is encased in a glass chamber. The vapors of alcohol, coming in contact with the platinum black, undergo a slow oxidation. The acetic acid, thereby formed, trickles down the glass walls of the receiver into a tray at the bottom of the contrivance.

(3) Large quantities of acetic acid are now produced by the dry distillation of wood. The apparatus employed consists of a suitable retort, with a furnace which heats it, and appropriate condensers and receivers. The wood being introduced into the retort and the temperature being raised by the fire, the cellulose of the wood undergoes decomposition. Many substances are produced. Among these are water, methyl alcohol (see page 66), tarry matters, and acetic acid. The acetic acid in its crude form, as thus manufactured, is known as pyroligneous acid. In this form it is used in some of the processes of calico printing.

For certain purposes, this crude acid is purified. Thus it is treated with lime in quantity sufficient to combine with the acetic acid. By this means a salt called acetate of lime is produced, but the tarry matters are still mingled with it. The mixture of acetate of lime and its impurities, is subjected to a heating or roasting process sufficient to char the impurities and yet leave the acetate uninjured. Subsequently the acetate is decomposed by the use of sulphuric acid or hydrochloric acid. When sulphuric acid is employed, the reaction produces not only free acetic acid, it also produces sulphate of lime. The latter is a thick pasty substance. The pasty mass may be subjected to pressure in bags, whereby the liquid containing the acetic acid is squeezed out of the mass. When hydrochloric acid is used, a very soluble calcium chloride is produced. The liquid mixture *from this operation* is usually introduced into the retorts and distilled. Acetic acid going off in the form of vapor, is afterward condensed in suitable coolers and brought to the liquid form.

(4) When the metallic salts called acetates are acted upon by suitable acids, acetic acid is liberated. The principle of this operation is very simple. It is the same as that just presented in the description of the purification of pyroligneous acid. Practically any salt of acetic acid may be employed.

Acetic acid when pure is a colorless liquid of a distinctly acid taste and smell. Upon the addition of suitable amounts of heat, it may be changed into vapor; while, under the influence of cold, it condenses to a solid.

Acetic acid combines with most of the metals to form the salts known as acetates.

Steps by which the rational formula of acetic acid is secured. The following statement is introduced as an illustration of methods employed in organic chemistry for discovering the molecular constitution of bodies :

1st. Direct organic analysis has shown that the empirical formula of acetic acid is $C_2H_4O_2$.

2d. With potassium, and other monad metals, acetic acid forms but *one* acetate; in this *one-fourth* of the hydrogen of the acid is expelled by the metal.

Then one atom of hydrogen is different in function from the other three atoms.

Then acetic acid may be written, $H \cdot C_2H_3O_2$.

3d. By electrolysis of potassium acetate, two different carbon compounds are liberated : ethane, C_2H_6, and carbon dioxide, CO_2. The reaction is believed to be in effect : $KC_2H_3O_2 = K + CO_2 + CH_3$. (The liberated potassium acts on the water and carbon dioxide; the methyl polymerises into ethane, $2CH_3 = C_2H_6$.)

Then one atom of carbon in acetic acid is closely connected to oxygen and one to hydrogen.

Again, acetates readily yield acetone (whose formula has been made out otherwise to be $CH_3 \cdot CO \cdot CH_3$). And acetone readily yields acetic acid again, changes which evidently do not profoundly disturb molecular arrangement. Now acetone, when treated with chlorine forms dichlor acetone, $CH_3 \cdot CCl_2 \cdot CH_3$, a compound whose structure is not substantially different from that of acetone.

These facts confirm the opinion that acetic acid holds the group carbonyl, CO.

Then acetic acid may be written, $H \cdot CO \cdot CH_3O$.

4th. When phosphorus trichloride acts on organic bodies it often withdraws hydroxyl, HO. When acting on acetic acid it withdraws one-fourth of the hydrogen present and one-half of the oxygen present :

$$H \cdot CO \cdot CH_3O + PCl_3 = CH_3 \cdot CO \cdot Cl + POCl + HCl$$

Here then, hydroxyl, HO, has been withdrawn.

This shows that probably acetic acid contains the group HO.

Then acetic acid may be written $HO \cdot OC \cdot CH_3$.

5th. By graduated action of chlorine on acetic acid, three-fourths of the hydrogen present are replaced step by step — but the last fourth is not so replaced. The three compounds produced are acids but slightly differing from acetic acid; they are

Monochloracetic acid, $HO \cdot OC \cdot CH_2Cl$
Dichloracetic   " $HO \cdot OC \cdot CHCl_2$
Trichloracetic   " $HO \cdot OC \cdot CCl_3$

These show, *first*, that the acetic acid has not been disturbed structurally, and *second*, that three atoms of hydrogen, while different in function from the fourth atom, are practically equivalent, one to another.

Then three atoms of hydrogen do not need to be separated in the formula.

Then acetic acid may have its formula stand as $HO \cdot OC \cdot CH_3$.

(In addition, there are a great many other chemical grounds for the decision reached.)

Acetate of lead, sometimes called sugar of lead, is largely used in the arts. It is ordinarily prepared by dissolving lead oxide, called litharge, in acetic acid. The acetate of lead formed separates out in well defined crystals. Two kinds of acetate of lead appear in commerce : the one, somewhat impure, called brown sugar of lead ; and the other, a higher grade, called white sugar of lead. Acetate of lead is largely employed in the manufacture of the acetates of aluminium and of iron for use in calico printing.

Aluminium acetate is produced by double decomposition between either aluminium sulphate or alum and acetate of lead. The lead and the sulphuric acid radicle combine to form plumbic sulphate, a white precipitate, which deposits at the bottom of the vessel. The other constituents form aluminium acetate which remains in the liquid. This liquid goes by the name of *red liquor* in calico printing because it is largely used as a mordant in producing red and pink colors.

The term *mordant* is ordinarily employed as a name for a mineral substance which has the power of chemically uniting with vegetable or animal dye stuffs to produce a new compound, the latter often possessing a color far different from that of its components. When cloth is treated first with a mineral mordant and then with a vegetable or animal dye stuff, the new colored compound is formed in, upon, or between the fibres of the textile material. The color is usually firmly fixed there, and does not wash out as a mere stain of coloring matter would. The principal kinds of dyeing involve, therefore, the use of mordants.

Now, *aluminium compounds are generally excellent mordants.* The aluminium acetate, or red liquor is oftener employed partly on account of the property of aluminium compounds just mentioned and partly because the *acetic acid is very favorable on account of its volatility.* In calico printing, red liquor mixed with starch is printed from an engraved roller upon cotton cloth. The whole is thoroughly dried and then is subjected to a further heating sufficient to expel most of the volatile acetic acid. The aluminic oxide or other compound still remaining in the cloth is in a suitable condition to act as a mordant ; for, if the goods are

now dipped in a solution containing alizarin or other suitable animal or vegetable dyestuff, chemical action quickly proceeds and the cloth is dyed.

Ferrous acetate is often used in calico printing in the form of a liquid called black liquor or iron liquor. Iron compounds are very favorable for use as mordants, vast quantities being used, in various forms of the dyer's art, chiefly for producing blacks or other dark shades. Iron liquor is usually manufactured by steeping iron filings in crude pyroligneous acid. The acetic acid quickly attacks the iron, forming an acetate. Considerable heat is evolved, and this favors further solution of the metal.

In calico printing, acetate of iron mixed with starch into a paste, is often printed at the same time as red liquor. Even other pastes may be printed simultaneously with these. As many as twenty different pastes may be applied to calico at the same time by the use of different rollers. These different pastes, each being applied in proper spots or on proper places, side by side or alternating, or in some cases overlapping, are subsequently dried thoroughly, as already described in case of red liquor. When the cloth is brought into the dye tub, the different mordants combine, according to their affinities, with one or several dye stuffs present, and thus produce a variety of different colors and designs upon the cloth. Madder root has long been employed for the preparation of calicoes in accordance with the principles here stated. Indeed, the general method has long been known as madder dyeing, and the goods are often spoken of as madder styles. Of late years, a wonderful improvement has been introduced whereby the starch paste, the mordant and the dye stuff are printed on the cloth at one operation — chemical combination, however, being prevented by suitable methods. The cloth, after drying, does not show its proper final coloring. The complete result is brought about by suspending the cloth of this stage in a large iron chamber and then subjecting it to high pressure steam — the heat and moisture furnishing the conditions necessary for chemical union of mordant and dye stuff. The true dyeing operation goes on under these conditions of steaming, and thus the proper colors are developed without the cloth ever being dipped into the old-fashioned dye tub.

Propionic acid, $HOOC \cdot C_2H_5$. This acid exists in certain fruits, in perspiration, in crude wood vinegar.

It may be prepared by the action of sulphuric acid and potassium dichromate on propyl alcohol, C_3H_7OH.

It is liquid at ordinary temperatures. It has a sharp odor.

Butyric acid, $HOOC \cdot C_3H_7$ (2 forms possible). Butter contains a glyceride of butyric acid ; when the butter turns rancid, a portion of the acid is set free.

It is usually prepared by fermentation of calcium lactate; calcium butyrate is formed and later from this butyric acid is separated.

It is a liquid having a sharp, rancid odor.

It readily forms salts with the metals and with the alkyl radicles. Of these, ethyl butyrate has a very aromatic and fruit-like odor. On this account the substance is prepared in the arts for use as a flavoring extract for certain kinds of confectionery.

Valeric acid, $HOOC \cdot C_4H_9$ (4 forms possible). It occurs in crude wood vinegar. It may be obtained from valerian root by distillation.

It is a liquid having a sharp odor resembling that of butyric acid.

Caproic acid, $HOOC \cdot C_5H_{11}$ (8 forms possible). Certain forms of this acid exist in butter whether made from cows' milk or from goats' milk. It also exists in certain other fatty substances, for example, in cocoanut oil.

Oenanthylic acid, $HOOC \cdot C_6H_{13}$ (17 forms possible). Acids of this set are produced by certain kinds of fermentation.

The acids are either liquids or easily melted solids.

Caprylic acid, $HOOC \cdot C_7H_{15}$. The normal acid exists as a glyceride in butter, in cocoanut oil. It exists free in fusel oil (a product of the fermentation of grain), in certain kinds of rank cheese.

The acid forms crystals at ordinary temperatures.

Pelargonic acid, $HOOC \cdot C_8H_{17}$, exists in *pelargonium roseum.* *Capric acid*, $HOOC \cdot C_9H_{19}$, exists in butter, cheese, cocoanut oil, etc. *Undekylic acid*, $HOOC \cdot C_{10}H_{21}$, may be prepared from certain other organic compounds. *Lauric acid*, $HOOC \cdot C_{11}H_{23}$, exists in combination in bayberry wax. *Tridekylic acid*, $HOOC \cdot C_{12}H_{25}$, may be prepared from other organic compounds. *Myristic acid*, $HOOC \cdot C_{13}H_{27}$, exists in certain vegetable oils. *Isocetic acid*, $HOOC \cdot C_{14}H_{29}$, exists in the oil of certain seeds.

Palmitic acid,	$HOOC \cdot C_{15}H_{31}$ ⎫	These acids exist, in the state of
Margaric acid,	$HOOC \cdot C_{16}H_{33}$ ⎬	combination known as glycerides, in a vast number of ani-
Stearic acid,	$HOOC \cdot C_{17}H_{35}$ ⎭	mals and plants.

The fatty or oily matters, having been separated by heating and straining or otherwise, are decomposed into the fat acids and glycerin.

The three acids mentioned are solids at moderately low natural temperatures. But they easily melt with slight heating. As their melting points are different, a mixture of the acids can be separated by partial cooling followed by pressing ; that is, if the *mixture* of the acids is held for some hours at a temperature at which one is solid while the others are liquid ; then by pressing, in a filter press or otherwise, the solid acid is retained as a cake, while the liquid ones pass through. Then the process may be repeated and a more complete separation secured.

Stearic acid is used in the manufacture of candles.

The three acids mentioned (and some others beside) are capable of forming true salts (soaps) with metals or their oxides or hydroxides. Some of these soaps are soluble in water, alcohol, etc., and some are insoluble. They will be discussed in brief under the title, soap.

Oils and Fats.

Before discussing the true oils and fats, glycerides, some comment on the word oil is demanded.

Oil of vitriol, petroleum oil, oil of lemons, lard oil, are substances in whose names the word oil was incorporated from a *superficial* resemblance of the compounds. Chemical study has shown, however, that the substances mentioned are very different. *Oil of vitriol* is not an organic compound at all, and resembles the other substances mentioned merely in the way in which it flows when poured. Several of the other oils mentioned resemble one another in facts like that of producing a translucent spot on paper. *Petroleum oils* consist chiefly of different hydrocarbons of the paraffin series mingled together. The *oil of lemons* belongs to a class of substances called volatile or essential oils. It has the composition $C_{10}H_{16}$. It is a hydrocarbon of the 10-carbon series, and should in no very distinct chemical sense be classified with the other oils mentioned. *Lard oil* belongs to the group of fatty oils known as *glycerides*. They are organic salts and may be classed as *esters*. They are compounds of glycyl and certain characteristic fatty acids. Most natural fats contain more than one glyceride. As early as 1820, Chevreul made a careful examination of natural fats. As a result, he declared that they consist of mixtures of organic salts, the salts being generally compounds of certain acids — of which he mentioned stearic acid and oleic acid, combined with glycerin.

Special glycerides have received names terminating in *in;* thus glycyl stearate is called stearin, glycyl palmitate is called palmitin, glycyl margarate is called margarin.

Distribution. Oils and fats are produced for commercial use from a large number of animals, as from fishes and the whale, from hogs, from sheep, and from beef cattle (and even horses), also from a large number of different vegetable matters, as from olives, the cotton seed, palm nuts, etc.

Preparation of fats. Animal matters, containing a certain amount of fat, are *rendered;* that is, they are heated in a variety of ways, subjected to action of hot water or steam, or both, and the fat is at length skimmed from the other matters.

Tallow oil is produced by melting ordinary tallow and then cooling it very slowly in what is called a *seeding room.* In this room the melted fat is placed in wooden cars lined with zinc, and the room is maintained at a temperature of 80° to 90° F. Little by little, the stearin separates out as crystalline flakes. The mixture of soft fats and hard fats is afterward placed in bags and pressed. The softer are expelled and they form the tallow oil of commerce, chiefly used for lubricating, occasionally for soap.

Lard oil is separated from lard by a process similar to that detailed for tallow oil. It is principally used for lubrication.

Bone grease is used in inferior soaps. The soap retains some color and a certain offensive odor. The latter must be disguised by scenting, unless the soap is to be used for manufacturing purposes. In the latter case a somewhat offensive odor is not objectionable.

Palm oil has been very largely used in the manufacture of soaps. It is obtained from the fruit of trees growing on the west coast of Africa, The fruit is of about the size of a small plum and it contains an outer pulpy mass and an inner kernel. From the pulp is obtained palm oil ; from the kernel is obtained palm-nut oil, or palm-kernel oil. The general process employed by the Africans for obtaining palm oil is as follows : The nuts are piled in heaps, and then subjected to a fermentation which goes on spontaneously, whereby certain of the constituents soften. Next they are thrown into pits lined with stone, where they are pounded until they form a pulp. In the succeeding stage the soft mass is put into water which is boiled. The oil rises to the sur-

face and is skimmed off. Sometimes this oil is squeezed through bags in order to accomplish a sort of filtration. The oil as it appears in commerce is a solid fat of the consistence of butter. It has an orange or golden yellow color, although the color varies in different varieties of oil. The oil has an agreeable odor which the soap made from it continues to afford. The soap has a color varying from yellow to orange according to the color of the original oil. Sometimes the oil is submitted to a chemical bleaching. About one hundred pounds of nuts afford about one gallon of oil. Many varieties of palm oil are brought to European parts. While they are prepared by different processes, the operations are substantially those already stated.

Cotton-seed oil. Each seed of cotton may be said to contain a drop of oil. Attempts to crush cotton-seed and extract oil from it were made in the State of Mississippi as early as 1834; that experiment and a subsequent one made in 1847, resulted in heavy pecuniary losses. More successful attempts were made in 1855, but the War of the Rebellion checked the progress of the industry. Of late, however, the business has progressed until now it has assumed great commercial importance. At present the seed is sold at a price equalling about $4.00 per bale of cotton. During the season of 1892 and 1893 seed equivalent to 2,500,000 bales of cotton was crushed ; this must represent a distribution of about $10,000,000 to cotton planters from seed alone.

This oil is employed in a variety of ways by bakers and families for shortening; also in the manufacture of soap; as a constituent of butterine; as a salad oil; as a basis for liniments; in miners' lamps (an Ohio law requires the use of this oil in mines.) Beside these there are many other uses in trade. Cotton-seed oil, however, is not satisfactory for household illumination, nor can it be used in lubrication; it thickens too readily by oxidation in the air.

The cotton-seed meal, from which the oil has been pressed, is used as a food for cattle, and to some extent as a fertilizer. The hulls are often used as fuel, the ashes (which contain a considerable quantity of potassium compounds) being subsequently employed as a fertilizer. The hulls have also been used to some extent in the manufacture of paper.

Blown oils. When certain oils that are not very good dryers, cotton-seed oil for example, are subjected to a blast of air at a temperature of about 200° C., for several hours, they undergo a marked change. They are called "blown" oils. Their viscosity is very much increased and they are better fitted for lubricating

use, especially when mixed with petroleum products. They also serve for the preparation of imitation leather, leatherette, linoleum, and similar materials.

Bleaching of oils. The *simplest* method of bleaching oils (applicable especially to the thicker ones, like palm oil) consists in a mere melting which permits solid matters to subside. This process may be supplemented to advantage by straining. A *second* method involves exposure to the sun in shallow tanks under glass windows such as are used in plant houses. A *third* method involves the use of a current of steam driven through the oil. A *fourth* method consists in blowing air through the oil or the melted fat. A *fifth* method, and one largely used, employs potassium dichromate and hydrochloric acid. Dichromate, dissolved in a small amount of water, is mingled with the heated oil. Constant stirring is employed. A proper amount of hydrochloric acid is now added, the entire mixture being again thoroughly agitated. The chromium compounds produced liberate oxygen which attacks certain of the coloring matters present. Subsequently the mass is treated with a large quantity of water, is agitated and stirred again. The water dissolves the bleaching materials that have been added, but it allows the bleached oil to come to the surface, whence it is drawn off. A *sixth* method involves the use of liquid chlorine. This substance is sold in drums, of course capable of standing great pressure. In using the chlorine a portion of it is passed into water and this solution is agitated with the oily material. After the bleaching is completed, more water may be added, and finally the oil may be drawn from the surface. Even soap may, under proper conditions, be bleached by liquid chlorine.

Uses of oils and fats. Oils and fats have most wide-spread and important uses in trade. Briefly stated, their principal uses are as follows : As food and in cooking other food (butter, lard, olive oil, cotton-seed oil, oleomargarine) ; as soap stock (tallow, cotton-seed oil, olive oil, and in general, almost any animal fats) ; as an illuminant, as candles or in lamps (lard oil, sperm oil) ; as lubricating material (lard oil, sperm oil) ; as a filling for leather (many inferior kinds of grease, like fish oils) ; as a source of glycerine (many kinds of oil) ; as a material for use in paints, oil-cloth, etc. (the *drying oils* exclusively, as linseed oil).

Stearin, or glycyl stearate, is a hard fat which is separated from the softer fats (after melting the mass) by gently lowering them in temperature in a room provided for the purpose. The stearin separates in crystals, while the soft fats remain liquid. In due time the mixture, being pressed in cloth bags, allows the softer fats to flow away while the harder remain as a white mass called stearin. The process is carried out on a large scale in the manufacture of artificial butter.

Oleomargarine, or butterine, consists essentially of *easily melting fats*, from which the harder fats have been separated by a process similar to that just described. The harder material, or stearin, is sold for the manufacture of candles, also for mixing with lard which is to be used in hot climates; thus the lard is kept at a satisfactory consistency. The oleo oil, after straining from the press, is mixed with some milk or cream (to give it the buttery flavor) with some coloring matter (to impart a yellow shade) and then, while still liquid, is thoroughly agitated with cracked ice. After the fats have hardened, a comparatively large amount of salt is introduced — this prevents the sense of taste recognizing readily the true flavor of the fats.

In natural butter made from cream, there exist certain fats which melt very readily at the temperature of the mouth. There exist certain others that by reason of their volatility, afford the peculiar flavor and odor of true cows' butter. In making artificial butter, the effort of the manufacturer is, first, to furnish a butter that is soft. Thus, when placed in the mouth, it melts easily and does not produce the tallowy impression associated with those fats which contain stearin. The essential chemical difference between artificial butter and real butter consists in the fact that the former lacks the volatile organic acids which give to cows' butter its agreeable flavor.

Soap. Soap is essentially a salt formed by the union of some metallic base with some organic fat acid. Ordinary hard soap is substantially a mixture of oleate, palmitate, and stearate of sodium. As a matter of fact, most laundry soaps contain resin in the form of resinate of sodium. Sometimes adulterants are employed, of which sodium silicate may be mentioned. It is said that many fine toilet soaps contain in addition sugar — sometimes even as much as twenty-five per cent.

The general principles involved in the manufacture of soap may be presented as follows: A solution of sodium hydroxide is

produced from that solid alkali called "caustic," at present manu-
factured on an enormous scale (it is poured while melted into
iron or steel drums). In the soap factory, the iron is stripped off
from the sodium hydroxide, and the solid caustic is thrown into
the water in which it is to dissolve. Next, fat is added, and the
mixture of fat and alkali is boiled. Decomposition ensues,
whereby, in place of glycyl stearate for example, sodium stear-
ate is produced, glycerin being liberated and dissolved in the
water present. Soap has now been produced, but it is in a liquid
form, that is, dissolved in water. Common salt is added to the
mass, whereupon the soap separates and gathers as a kind of curd
at the top of the liquid. The salt water containing other impuri-
ties is now drawn away; the soap then receives a second boiling,
with more sodium hydroxide. By and by saponification becomes
complete. Upon allowing the mixture to stand, a dark colored
liquid settles to the bottom, and the soap comes to the top.
The latter is ladled out into "frames" where it dries to a suffi-
cient extent to enable it to assume a solid condition. The frames
being removed, the block of soap is cut, by means of wires, into
bars of suitable size. In case of the finer soaps, the small blocks
first produced are pressed or shaped by machinery to the form
desired.

Marseilles soap, or castile soap, is usually manufactured from
olive oil. It is very carefully prepared and thoroughly boiled so
as to accomplish the complete saponification of the oil. The
mottled castile soap contains an admixture of ferrous sulphide or
some other ferrous salt. This substance, upon coming to the air,
oxidizes and thus changes from the green to the red color.

Cotton oil soap. Within a few years, vast quantities of oil have
been expressed from cotton seed; and this oil is very largely used
for the manufacture of soap.

Most solid soaps contain large amounts of water. Twenty-five per cent. is
not an uncommon amount, and some kinds are said to contain as much as
seventy per cent. Soap, if thoroughly dried, assumes the form of a powder.
In this form — with or without addition of dry sodium carbonate — it is very
largely used as a soap substitute.

2-Oxygen Acids of the Formula $C_n H_{2n-2} O_2$.

These acids are usually designated as of the acrylic series. A
great number of them are known. Only one will be mentioned.

Oleic acid, $C_{18}H_{34}O_2$. It occurs in combination with glycyl in a great many soft fats, and to some extent also in the harder fats, as the substance called olein.

Olein is associated with stearin, margarin, and palmitin, in practically all the ordinary crude oils and fats which are employed in the arts. Olein is discussed here, however (and not with palmitin, margarin, and stearin,) because oleic acid has a slightly different carbon linkage from that prevailing in the other common acids of fats.

2-Oxygen Acids of the Formula $C_n H_{2n-4} O_2$.

Linoleic acid, $C_{16}H_{28}O_2$. This acid (existing as a glyceride in linseed oil) is an oily liquid.

Drying oils. Certain vegetable substances yield fatty oils which are true glycerides and which have the remarkable power of absorbing oxygen from the air and thus producing solids. Linseed oil is the best example. It is obtained by mechanical pressure from the seed of flax. Its oil is composed of glycerin united with several special fatty acids, the principal one being known as linoleic acid. When linseed oil is spread over the surface of wood, paper, or any solid, it absorbs oxygen from the air, forming what is called a skin. The oxidation may go on gradually and yet eventually produce a solid mass. In oil painting, linseed oil is used; and the so-called drying of the paint is due to the operation just described. It does not represent any evaporation like that taking place when water colors are applied to paper. It represents, instead, an absorption of something from the air, namely, oxygen. If linseed oil in a tank is subjected to a current of air forced through it, it is easily shown that oxidation goes on, by the subsequent analysis of the product and by the fact that the original oil rises in temperature and increases in weight. It also becomes very thick and pasty, producing a quantity of gum that may be employed in many ways in the arts.

Linseed oil is often boiled with certain compounds of lead, in which case a quantity of soap is formed which may be called lead linoleate. If red lead is used in the boiling operation, the oxygen of this highly oxidized compound assists in the oxidation of the oil.

In order to make oil paint spread easier, it is often thinned with certain solvents like turpentine or petroleum naphtha. When such thinned liquids are employed for painting purposes, of course the volatile solvent evaporates, leaving a thin layer of the thicker oil behind.

3-Oxygen Acids of the Formula $C_n H_{2n} O_3$.

Carbonic acid, CH_2O_3, or $HOOC \cdot OH$. This acid has a theoretical rather than an actual existence. Its formula is deduced from those of its salts. Its anhydride, carbon dioxide, CO_2, is

well known ; it is usually discussed with the compounds of the non-metals. The acid is mentioned here mainly for purposes of classification.

Glycollic acid, $C_2H_4O_3$, or $HOOC \cdot CH_2OH$. This acid is produced by oxidation of glycol, ethylene alcohol, $C_2H_4(OH)_2$, somewhat as acetic acid is produced by oxidation of ethyl alcohol, C_2H_5OH.

The acid is a crystalline solid.

Lactic acid, $C_3H_6O_3$, or $HOOC \cdot CHOH \cdot CH_3$. This is the acid of sour milk. It may be formed, however, from a number of other substances. Thus the proper fermentation of starch and of glucose gives rise to it. It also exists, in some forms of dyspepsia, in the gastric juice. It is produced by the souring of certain vegetables. Lactic acid appears to be the product of a specific fermentation called the lactic fermentation, and this fermentation is carried on under the influence of a special microbe called *bacterium acidi lactici.* A special method has lately been invented for producing a pure culture of the lactic ferment, then allowing it to act upon glucose made from corn starch. There is thus produced a lactic acid comparatively free from by-products.

It has been proposed to use such lactic acid in some processes of dyeing of textile fabrics as a substitute for certain other organic acids, notably oxalic and tartaric acids.

Lactic acid, lactates, and many other derivatives of lactic acid, have been carefully studied for the purposes of theoretical chemistry.

3-Oxygen Acids of the Formula $C_n H_{2n-2} O_3$.

Ricinoleic acid, $C_{18}H_{34}O_3$. This substance occurs in combination in castor oil and some other oils. Like other fatty substances, it exists here as a glyceride.

Ricinoleic acid of castor oil forms with sulphuric acid a sulphonic acid. This substance is considerably used in dyeing and calico printing, particularly in connection with alizarin. It is often called "alizarin assistant." With the aluminous mordants, it seems to form favorable compounds from which the alizarin can subsequently withdraw the alumina so as to produce the desired red color upon cloth.

4-Oxygen Acids of the Formula $C_n H_{2n-2} O_4$.

Oxalic acid, $C_2H_2O_4$, or $(HOOC)_2$, occurs in nature in certain plants ; as for example, in sorrel, *oxalis acetosella.*

Oxalic acid may be manufactured by the action of nitric acid upon sugar.

This acid is now produced on a large scale from sawdust of certain kinds, especially pine, by heating it with solid potassium hydroxide. (Sodium hydroxide alone will not accomplish the change.)

Oxalic acid readily forms white crystals containing two molecules of water. It is a strong acid, compared with other organic acids ; in considerable quantities, it is very poisonous.

Oxalic acid is largely used in certain textile industries ; as in calico printing and in wool dyeing. Here it is strong enough to accomplish the decomposition as desired ; but it does not, like the inorganic acids, injure the fibre to which it is applied.

Oxalic acid forms a large number of salts, some of them considerably used in the arts. Calcium oxalate is a white substance, insoluble in water. It is in this form that calcium is ordinarily precipitated in chemical analysis.

Ammonium oxalate, a white crystalline salt, soluble in water, is largely used in chemical analysis for the recognition of calcium by the method already suggested.

Malonic acid, $C_3H_4O_4$, or $HOOC \cdot CH_2 \cdot COOH$. This is a colorless crystalline solid.

Succinic acid, $C_4H_6O_4$, or $HOOC \cdot CH_2 \cdot CH_2 \cdot COOH$. Succinic acid was originally obtained by the distillation of amber. It has since been learned that it may be produced from certain varieties of lignite. It is said to exist also in lettuce and certain other vegetables. It has often been reported as existing in unripe grapes.

At present it is well recognized that succinic acid may be produced by certain purely chemical transformations, and also by certain fermentations under the influence of a special and appropriate microbe. Thus, malic acid, the acid of certain other fruits beside the apple, may afford succinic acid by an appropriate fermentation. This is not difficult to comprehend chemically, because malic acid is oxysuccinic acid.

Succinic acid forms many succinates ; as ammonium succinate, which forms transparent crystals soluble in water and which is used somewhat in chemical operations. Thus, it is employed occasionally in the precipitation of iron. It then forms a ferric succinate which is a gelatinous precipitate.

7

4-Oxygen Acids of the Formula $C_nH_{2n-4}O_4$.

Fumaric acid, $C_4H_4O_4$, or   HOOC·CH
                                    HC·COOH

Maleic acid, $C_4H_4O_4$, or   HOOC·CH
                                    HOOC·CH
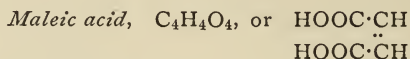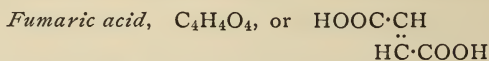
Both of these acids are produced by the dry distillation of malic acid, $C_4H_6O_5$. They have different chemical properties, although they have the same empirical formula. They are believed to be geometrical isomers; that is in the two cases the carboxyl groups are distributed on *different sides* of the doubly linked carbon atoms, an arrangement that is partly suggested by the formulas printed above, but is better displayed when these carbon atoms are represented by tetrahedrons.

5-Oxygen Acids of the Formula $C_nH_{2n-2}O_5$.

Malic acid, $C_4H_6O_5$, or HOOC·CH₂·CHOH·COOH. Malic acid has long been recognized as existing in certain sour fruits; as, pears, apples, gooseberries, barberries, and many others.

Malic acid is generally prepared from the berries of the mountain ash. It is not much employed in chemistry, although it forms many malates and substitution compounds.

6-Oxygen Acids of the Formula $C_nH_{2n-2}O_6$.

Tartaric acid, $C_4H_6O_6$, or HOOC·CHOH·CHOH·COOH. This substance is properly the acid of grapes. It appears to exist in grape juice in the form of an acid potassium tartrate. While the source just mentioned is the chief one employed in the production of the tartaric acid required in the arts, this acid is found in many other plants.

It is worthy of note at the outset that there appear to be four kinds of tartaric acid, all having the same empirical formula.

First, ordinary or dextrotartaric acid. Aqueous solution of this acid has the power of turning the plane of the polarized ray to the right.

Second, laevotartaric acid. This substance, when in aqueous solution, has the power of turning the plane of the polarized ray to the left.

Third, racemic acid. This acid is optically inactive. It is produced when equal quantities of the dextro- and the laevo- acids are dissolved in water, brought together, and then crystallized. Racemic acid may afterward be resolved into the two optically active tartaric acids.

Fourth, mesotartaric acid. This is optically inactive.

The peculiarities of tartaric acid have been carefully studied, first by Louis Pasteur, many years ago, since by others. At present the differences are considered as due to geometrical isomerism and they are explained on the basis of the modern theories of stereo-chemistry. This involves the idea that the carbon atom may have its four points of attraction not in one plane but at four points corresponding to the apexes of a tetrahedron. Then two or more atoms of carbon may be connected by apexes or by edges of the imagined tetrahedron. Then radicles attached at the other solid angles of the tetrahedron may be disposed differently in space. In case of asymmetric carbon atoms the attached radicles may have clearly two different relative positions differing somewhat as the parts of a real object differ in position as compared with these parts as they appear when reflected in a mirror.

The different varieties of tartaric acid are capable of forming different tartrates as well as racemates.

In the course of the fermentation of wine, the generation of alcohol by decomposition of sugar forms a solution that tends to precipitate certain of the tartrates. At the bottom of wine casks a sediment forms. It is called argols or wine lees, or crude tartar. It consists chiefly of acid potassium tartrate, but it also often contains calcium tartrate. From this material is manufactured tartaric acid and the various tartrates used in medicine and in the arts.

Tartaric acid may be produced by acting upon the crude tartar with chalk; thereby calcium tartrate is precipitated. This precipitate is subsequently decomposed by sulphuric acid, thus forming calcium sulphate and liberating tartaric acid. The latter substance separates in crystals when the clear liquid containing it is allowed to cool. Tartaric acid has also been produced synthetically.

Tartaric acid is easily decomposed by heat and by many chemical reagents. Thus it may be broken up into various modified forms of tartaric acid : it may produce acetic acid, formic acid, carbonic acid, and several other substances.

Tartaric acid or its salts are considerably used in medicine. The acid is largely used in dyeing and calico printing. Reference has already been made to its use in calico printing for decomposing yellow prussiate of potash, thus forming Prussian blue upon the cloth. In dyeing certain scarlets upon wool, tartaric acid or acid potassium tartrate is often employed; and while other acids may be used in its stead, they do not fully replace it.

Two of the most important salts of tartaric acid are the acid potassium tartrate called cream of tartar, and the potassioantimonylic tartrate called tartar emetic.

Cream of tartar. This substance is very largely employed in the United States and Canada in the production of baking powders. Practically speaking, baking powders are mixtures of three dry substances. The first is a dry acid compound. It may be cream of tartar or an acid phosphate. The second substance is hydrosodium carbonate. The third substance is flour or starch. While these three substances are dry, no chemical reaction takes place. As soon, however, as they are brought in contact with water, the first two dissolve and the starch softens. The first two react in such a way as to liberate a large volume of carbonic gas. If the operation takes place in presence of an ample supply of wheat flour or similar material, the paste so produced is inflated by a multitude of little bubbles of carbonic gas. If this paste is quickly heated in an oven, that is, baked, the cell walls are thereby hardened. Thus, what is called light bread is produced. It may be noted that in the fermentation of bread by means of yeast or leaven, the starch or flour, under the influence of the yeast microbe, undergoes decomposition into carbon dioxide and alcohol. The liberation of carbon dioxide in minute portions throughout the dough or other paste accomplishes an inflation similar to that which is produced by the baking powders as just described. With baking powders the inflation is quicker. It must be remembered, however, that the baking powders leave in the bread certain salts which were formed at the time of the liberation of the carbonic gas.

Tartar emetic, in doses of a few milligrammes, has medical effect; in slightly larger doses, it acts as an emetic; while, if the dose is still further increased, it acts as a poison, sometimes with fatal results.

Citric acid, $C_6H_8O_7$, or $(HOOC)CH_2 \cdot (HOOC)COH \cdot (HOOC)CH_2$

$$HOOC \cdot CH_2$$
$$|$$
$$HOOC \cdot COH$$
$$|$$
$$HOOC \cdot CH_2$$
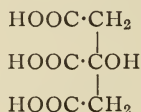
This substance is that which imparts the sour taste to lemons, limes, and certain other fruits. In the currant, raspberry, strawberry, cherry, and other fruits, citric acid exists together with malic acid.

Citric acid is manufactured in the form of a syrup and also in the form of transparent colorless crystals. It is produced in Sicily and the West Indies. The juice of the lemon, for example, being pressed out of the fruit, is first precipitated by the use of powdered chalk. Calcium citrate is formed and precipitated.

After this salt has been washed, it is decomposed by sulphuric acid which combines with the calcium, forming an insoluble calcium sulphate, and at the same time liberates the citric acid. The latter substance may then be separated in crystals by evaporation or cooling or the two combined.

Like several other organic substances commonly found in animals and plants, citric acid has been produced synthetically.

Citric acid forms many citrates, some of them used in medicine. Citric acid is considerably used in calico printing where a substance having mild acid properties is desired, but one which will not injure the goods. It is often printed on calico in the form of a paste, as what is called a "resist." At the points on the cloth where the citric acid is, the dyeing materials subsequently applied produce no color, owing to the action of the acid. By this means, white spaces may be left where the pattern demands it.

ALDEHYDES AND KETONES.

Aldehydes have the general formula, $R \cdot CO \cdot H$, while ketones have the general formula, $R \cdot CO \cdot R$. Thus an aldehyde is a ketone in which one of the alkyl radicles has been replaced by hydrogen; or a ketone in an aldehyde in which the principal atom of hydrogen has been replaced by an alkyl radicle.

Aldehydes.

Many aldehydes are known. They are generally formed by oxidation of corresponding alcohols. They are also formed by decomposition (under the influence of heat, with special conditions,) of certain salts of organic acids.

Most of the aldehydes are volatile liquids.

Among the general chemical properties of aldehydes are the following:

1. They are easily oxidized into organic acids.

2. They are powerful *reducing* agents; thus when added to certain solutions of silver salts they *reduce* the salts, precipitating the metallic silver in such a form that it forms a lustrous mirror on the inside of the glass vessel in which the operation is conducted.

3. Some of them form solid crystalline compounds with ammonia.

Formic aldehyde (called formalin) CH_2O, or $H \cdot CO \cdot H$. This substance is produced by oxidation of methyl alcohol. The method employed is to conduct a mixture of air and vapor of methyl alcohol over moderately heated platinum (either in the form of wire or sponge). The platinum determines an oxidation:

$$2CH_3OH + O_2 = 2H \cdot CO \cdot H + 2H_2O$$

2CH₃OH	+	O₂	=	2H·CO·H	+	2H₂O
Methyl alcohol		Oxygen		Formic aldehyde		Water
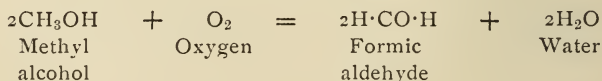
The substance is a volatile liquid.

A water solution of it is used in physiological laboratories for preserving and hardening animal tissues (it coagulates albuminous matters).

It is somewhat used as a disinfectant.

Acetic aldehyde (ordinary aldehyde) C_2H_4O, or $CH_3 \cdot CO \cdot H$. This substance is produced by the oxidation of ethyl alcohol. When vapor of ethyl alcohol mixed with air comes in contact with platinum sponge the alcohol is oxidized into aldehyde as well as into acetic acid (the latter represents a more considerable oxidation). Indeed, in making acetic acid from alcohol by such a process, care must be taken that aldehyde *is not* formed — it would occasion waste.

Aldehyde is also formed when ethyl alcohol is oxidized by potassium dichromate and sulphuric acid (a much-used oxidizing mixture).

$$2C_2H_5OH \quad + \quad O_2 \quad = \quad 2CH_3 \cdot CO \cdot H \quad + \quad 2H_2O$$

Ethyl alcohol	Oxygen	Acetic aldehyde	Water
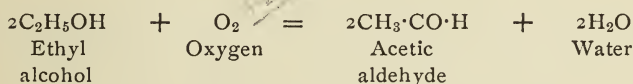
Acetic aldehyde is a colorless, volatile liquid, having a peculiar, etherial odor. (Inhalation of a considerable quantity of the vapor is injurious.)

Chloral, C_2HCl_3O, or $CCl_3 \cdot CO \cdot H$. Just as the oxidation of alcohol produces aldehyde, so its powerful chlorination produces chloral. A comparison of the formulas of aldehyde and chloral shows that the former corresponds closely with the latter, except that in the latter three atoms of chlorine take the place of three of the atoms of hydrogen in the other.

The well known form of chloral is the hydrate, $C_2HCl_3O \cdot H_2O$, a substance much used for inducing sleep. This effect of chloral hydrate is believed to be due to its change into chloroform in the animal system. Artificially, the alteration into chloroform may be produced by addition of an alkali. Thus,

$$C_2HCl_3O \quad + \quad KOH \quad = \quad CHCl_3 \quad + \quad KOOC \cdot H$$

Chloral		Chloroform	Potassium formate
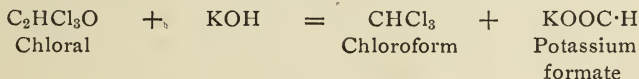
Ketones.

The general formula of the ketones, $R \cdot CO \cdot R$, at once suggests the possibility of two classes existing. (1) When the two alkyl radicles are alike the ketone is called *simple*. (2) When the two alkyl radicles are different the ketone is called *mixed*. Thus dimethyl ketone (ordinary acetone) $CH_3 \cdot CO \cdot CH_3$, is a simple ketone; methyl ethyl ketone, $CH_3 \cdot CO \cdot C_2H_5$, is a mixed ketone.

Ketones are produced from salts of organic acids and from alcohols.

Thus destructive distillation of calcium acetate yields a ketone, dimethyl ketone, ordinary acetone, $CH_3 \cdot CO \cdot CH_3$:

$$Ca(OOC \cdot CH_3)_2 \ heated \quad = \quad CH_3 \cdot CO \cdot CH_3 \quad + \quad CaCO_3$$

| Calcium acetate | | Dimethyl ketone | | Calcium carbonate |
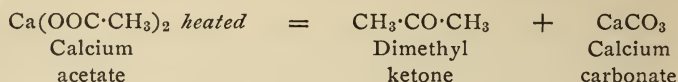
Oxidation of secondary alcohols yields ketones :

$$2(CH_3 \cdot CHOH \cdot CH_3) \quad + \quad O_2 \quad = \quad 2(CH_3 \cdot CO \cdot CH_3) \quad + \quad 2H_2O$$

Secondary
propyl alcohol
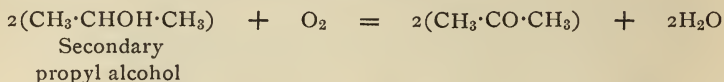
The ketones with smaller numbers of carbon atoms are volatile liquids, those with higher numbers are crystalline solids.

Acetone, dimethyl ketone, C_2H_6O, or $CH_3 \cdot CO \cdot CH_3$. This substance is a volatile liquid, having a peculiar odor.

It is prepared by the dry distillation of metallic acetates, as barium or calcium or lead acetate. It is also produced (along with methyl alcohol, acetic acid, and other compounds,) when wood, sugar, starch, gums, and other similar substances, are subjected to the process of dry distillation, with or without lime.

Acetone is somewhat used in the arts as a solvent.

CHAPTER XIV.

CARBOHYDRATES.

Introduction.

Sugar, starch, cellulose (woody fibre), and gums are somewhat typical substances. They represent a numerous and important class of bodies whose representatives are very widely distributed through vegetable matters (and to a far less extent in animal matters). These substances are compounds of carbon, hydrogen, and oxygen; and in many cases the hydrogen and oxygen are in the proper ratio to form water. These substances have been called carbohydrates. But they are not hydrates of carbon; they are not compounds of carbon and water; indeed there are members of the group, recently discovered, in which the hydrogen atoms bear to the oxygen atoms other ratios than $2:1$. However, they are still called carbohydrates for convenience. (Of course they must be carefully distinguished from hydrocarbons.)

All the indications lead to the belief that the carbohydrates are open chain compounds. The prevalence in carbohydrates of the group C_6 which is characteristic of aromatic compounds, and also the fact that benzene, C_6H_6, the typical aromatic compound, is easily derived from cellulose and from bituminous coal (itself distinctly derived from cellulose) point to some intimate relationship between carbohydrates and aromatic compounds.

In the majority of cases the molecular structure characterizing carbohydrates has not been satisfactorily made out; but within recent years several European chemists, notably Emil Fischer and B. Tollens, have made very great progress in this line. But there is still much doubt not only as to the proper rational formulas for carbohydrates, but even as to the exact empirical formulas.

Again, the correct arrangement and classification of these substances is uncertain. Many systems of naming have been proposed, but as these depend upon different theories of the composition and relationships of the bodies under discussion, no system of naming even has gained general acceptance.

Some of the reasons why the formulas of carbohydrates are not absolutely determined are the following:

1. Practically all of them are solids, not capable of assuming the gaseous state without decomposition. (But the gaseous form of a compound is almost the only one that reveals its molecular weight.)

2. The fact that they are solids suggests that they have large numbers of atoms in the molecule. (Of course this gives opportunities for many isomers and so creates uncertainty in a particular case.)

3. They are rather neutral in their chemical relations. (Now substances that do not readily form substitution compounds and the like, offer special difficulties in the way of fixing of their structures.)

4. When a given carbohydrate is decomposed by heat or other agencies, it generally produces a great many different products, and some of these are difficult of identification. (These facts operate somewhat like those already mentioned.)

5. It is by no means easy to build up carbohydrates synthetically; most of them are products of growing plants, and while in the plant, they appear to be produced by simple operations (that is, carbon dioxide of the air or of the soil, and water, form certain sugars, and these produce starches, gums, and woody fibre,) yet the plant physiology of the carbohydrates is not easy to fathom.

It must be stated, however, that in recent years a large number of sugar-like carbohydrates have been made artificially.

First Group. The Sugars.

1.   The sugars are widely distributed in plants; most sweet fruits and sweet vegetable juices contain one or more kinds of sugar; so do some animal products, as milk, which contains milk-sugar or lactose. (Of course honey is a vegetable product, for the honey bee merely collects the sweets from flowers.)

2.   Sugars are ordinarily prepared by extracting the juice from the plant (as in squeezing sugar cane) and then purifying and evaporating the juice. But some sugars are prepared chemically from other products.

3.   The sugars are sweet in taste, but some are sweeter than others; thus cane sugar is sweeter than milk sugar. (The artificial aromatic compound *saccharine*, 500 times as sweet as cane sugar, belongs, however, to an entirely different class.)

4.   Most of the sugars, when in solution, rotate the plane of the ray of polarized light; those which turn it to the right are designated as d (dextro) — to the left, l (laevo) — the optically inactive ones, i.

5.   Many sugars have a marked effect on Fehling's solution. This solution is essentially cupric sulphate acidified by tartaric acid and then rendered strongly alkaline with sodium hydroxide.

(Addition of sodium hydroxide to copper compounds usually gives rise to a precipitate of copper hydroxide. Tartaric acid and certain other organic substances have the power of preventing this precipitation, so that in this case, the sodium hydroxide, instead of precipitating the copper, dissolves it to a deep blue liquid.) The action of certain sugars upon Fehling's liquid is to withdraw oxygen from the copper compound and to produce a brick red precipitate of cuprous oxide, Cu_2O. If a sufficient amount of the sugar is employed, all of the copper may be thrown out of the liquid in this way.

6. In many cases caustic alkalies turn sugars and other carbohydrates to brown colored compounds.

7. Acids decompose sugars — dilute acids often produce what is called invert sugar. Concentrated nitric acid often produces saccharic acid and mucic acid, and eventually even oxalic acid.

8. Yeasts act upon some sugars and not upon others.

9. Phenyl hydrazine, $NH(C_6H_5) \cdot NH_2$, is one of the most important of reagents as respects carbohydrates.

The substance called hydrazine, $NH_2.NH_2$, may form certain substitution compounds; one of these is phenyl hydrazine, $NH(C_6H_5) \cdot NH_2$, or $NHPh \cdot NH_2$.

When phenyl hydrazine acts on aldehydes and on ketones it forms certain reduction products called hydrazones, thus:

> Acetaldehyde hydrazone is $NHPh \cdot N : CH \cdot CH_3$
> Acetone hydrazone   is $NHPh \cdot N : C(CH_3)_2$
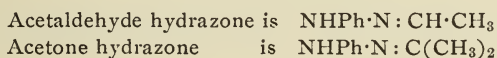
But phenyl hydrazine also yields hydrazones with sugars; the hydrazones may be changed to osazones (generally rather insoluble in water); thence to osones, which by nascent hydrogen may yield sugars, different it may be from the sugar used at the outset.

Conspectus of Sugars.

Triose. $C_3H_6O_3$. *Glycerose.* (Artificial.) Prepared by oxidizing action of bromine in presence of sodium carbonate on glycerol, $C_3H_8O_3$.

Tetrose. $C_4H_8O_4$. *Erythrose.* (Artificial.) Prepared by oxidizing action on erythrol, $C_4H_{10}O_4$.

Pentoses. $C_5H_{10}O_5$. *Arabinose.* (Artificial.) Prepared from certain gum arabics by action of dilute sulphuric acid. — *Xylose.* Prepared from certain vegetable gums by action of concentrated sulphuric acid.

Hexoses. $C_6H_{12}O_6$. (Many are artificial.) *a-Acrose.* Prepared from formic aldehyde, CH_2O, by action of magnesium oxide and sulphate with granulated lead.— *Formose.* Also prepared from formic aldehyde.— *Galactose*, d, l, i. Prepared from milk-sugar and other substances by various methods.— *Glucose*, d, l, i. d occurs in many sweet fruits. It is made artificially from starch by action of dilute sulphuric acid and otherwise.— *Gulose.* Artificial.— *Dambose.* Occurs in certain muscular tissues of animals.— *Fructose.* Occurs widely distributed in fruits.— *Mannose*, d, l, i. d occurs in certain nuts.— *Phenose.* Prepared from certain aromatic compounds of phenyl hydride, $C_6H_5\cdot H$.— *Sorbose.* Prepared by fermentation of the juice of berries of *mountain ash, sorbus.*— *Rhamno-hexose.*— (Many others.)

Heptoses. $C_7H_{14}O_7$. *Gluco-heptose.* Artificial.— *Manno-heptose.* Artificial.— *Rhamno-heptose.* Artificial.— (Many others.)

Octoses. $C_8H_{16}O_8$. *Gluco-octose.* Artificial.— *Manno-octose.* Artificial.

Nonoses. $C_9H_{18}O_9$. *Gluco-nonose.* Artificial.— *Manno-nonose.* Artificial.

. . . .

——. $C_{12}H_{22}O_{11}$. *Maltose.* Produced by action of malt upon starch (and otherwise).— *Lactose*, milk sugar. Exists in the milk of mammals and elsewhere).— *Sucrose*, cane sugar. Exists in juice of sugar cane, sugar beet, sugar maple, sugar palm, and in the nectar of flowers (in honey) and elsewhere. Usually it is found in nature mixed with other sugars, etc.— (Several others.)

——. $C_6H_{12}O_5$, $C_{18}H_{32}O_{16}\cdot 2H_2O$, $C_{18}H_{32}O_{16}\cdot 5H_2O$. These formulas present suggestions of many other sugars of different type from those above referred to.

Glucose, $C_6H_{12}O_6$ (d, l, i.)

This is the substance called dextrose, grape-sugar, starch-sugar.

The formula is supposed to be one of the three following :

$$
\begin{array}{lll}
\text{H} & \text{H} & \text{H} \\
\text{HC—OH} & \text{HC—OH} & \text{HC—OH} \\
\text{HC—OH} & \text{HC—OH} & \text{HC—OH} \\
\text{HC—OH} & \text{HC—OH} & \text{HC—OH} \\
\text{HC—OH} & \text{HC—OH} & \text{C}=\text{O} \\
\text{HC—OH} & \text{C}=\text{O} & \text{HC—OH} \\
\text{HC}=\text{O} & \text{HC—OH} & \text{HC—OH} \\
& \text{H} & \text{H}
\end{array}
$$
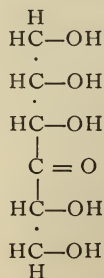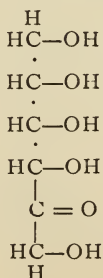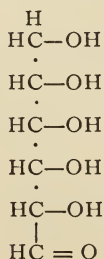
Glucose is widely distributed in nature in sweet fruits. It exists also in honey. In certain morbid animal processes, it is produced and excreted. In human beings this occurs in the disease called *diabetes mellitus.*

Glucose may be produced artificially by the action of certain dilute acids upon starch. In some parts of the United States the manufacture of such glucose is an important industry. Corn starch is heated gently with sulphuric acid until the chemical change has been accomplished. The excess of sulphuric acid is then removed by the addition of lime. Calcium sulphate is produced and appears as an abundant white precipitate. The pasty mass being strained in filter presses, affords a clear syrup containing the glucose. This syrup may be partly or wholly evaporated in suitable vacuum pans. If wholly evaporated, it leaves a white solid known in the trade as glucose. This material is largely used as a substitute for cane sugar, and occasionally as an adulterant for it. It cheaply replaces cane sugar in an enormous quantity of candies. Owing to its capacity for fermentation, it is also employed in the manufacture of beer and ale.

In the form of a syrup, it is largely used as a substitute for sweetening liquids such as molasses, maple syrup, and sugar house syrup.

Glucose is produced by the decomposition of many other sugars : thus cane sugar is decomposed by dilute acids :

$$C_{12}H_{22}O_{11} + H_2O \quad = \quad C_6H_{12}O_6 \quad + \quad C_6H_{12}O_6$$
$$\text{Cane sugar} \qquad\qquad \text{Glucose} \qquad \text{Laevulose}$$

Glucose is a reducing agent. It reduces cupric oxide in Fehling's solution to cuprous oxide. It also reduces certain mercury solutions to metallic mercury.

Laevulose or Fructose, $C_6H_{12}O_6$ (l.)

This substance exists in honey. It also exists widespread in the vegetable kingdom in fruits, sometimes with glucose, sometimes with cane sugar.

It is soluble in water; crystallizes; reduces Fehling's solution; it ferments with yeast.

Maltose, $C_{12}H_{22}O_{11}$ (d.)

This substance is formed by the action of malt on starch, an operation due to the existence in the malt of a peculiar unorganized ferment called diastase.

Maltose is soluble in water; it crystallizes; it reduces Fehling's solution; it ferments with yeast; it combines with phenylhydrazine.

Lactose (Milk Sugar), $C_{12}H_{22}O_{11}$ (d.)

This substance is produced in considerable quantity in Switzerland. The whey of milk is evaporated and the sugar is then crystallized from it upon threads hung in suitable vessels.

Milk sugar has attained a considerable consumption as a material for use by homœopathic physicians. It is also somewhat employed as an addition to cows' milk used in the feeding of human infants. (In this case, it seems to favor digestion far more than any addition of cane sugar.)

Lactose is soluble in water; it crystallizes; it reduces Fehling's solution; it does not ferment with pure yeast; common yeast ferments it into alcohol and lactic acid; by boiling with dilute sulphuric acid, it forms dextrose and galactose.

Sucrose (Cane Sugar) $C_{12}H_{22}O_{11}$ (d.)

Cane sugar, called sucrose. Sucrose is sweeter than the other true sugars and it crystallizes better. It is a most important article of human food. Sucrose, as well as the other carbohydrates, are looked upon as fat-producers in the animal economy rather than as muscle-producers. (For the production of muscle, nitrogenous food is necessary.)

Cane sugar, in a state of absolute whiteness and crystalline purity, as now used so largely by civilized beings, is a comparatively modern article of food. The sugar cane originated in the far East. In 1495, it was introduced into St. Domingo, and a few years later, into other parts of the West Indies. The introduction of sugar into Europe is usually considered to have been one of the results of the Crusades. It was originally esteemed a valuable medicinal remedy, and a little later a supreme luxury for the rich.

Sucrose is soluble in water, but only sparingly soluble in alcohol; it crystal-lizes; it melts without decomposition, but on further heating it changes to a brown substance called caramel; by influence of a small amount of warm dilute mineral acid it decomposes into dextrose and laevulose:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
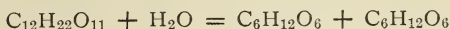
The process is described as *inversion* and the product is spoken of as *invert sugar;* sucrose does not reduce Fehling's solution; while it may be fermented by yeast, it does not do so readily or directly.

The following constitutional formula for cane sugar has been suggested :
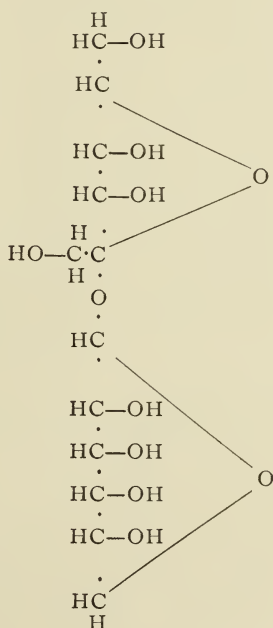
The chief commercial sources of sucrose are the *sugar cane* and the *sugar beet.* In the aggregate, considerable quantities of sugar are manufactured from the *sorghum plant,* from the sap of the *maple,* also from the sugar palm (which sends into commerce a crude sugar called *jaggery*). In the manufacture of crystallized cane sugar from any of these sources, the operations may be grouped in four stages: first, securing the vegetable juice; second, preliminary evaporation; third, decolorizing the

syrups; fourth, crystallizing the sucrose. The details of these operations vary considerably according to which of the four sources of supply is considered. Moreover, in preparing sucrose from one of these sources, different establishments employ slightly different methods.

First, sucrose from the sugar cane. After the cane has been cut, it is subjected to pressure by means of large rollers. Squeezed between these rollers, the sugary juice is expelled as a kind of syrup. This syrup contains in addition to sucrose certain other substances, particularly albuminous substances which afford conditions easily leading to such a fermentation of the juice as will produce *difficultly crystallizable* sugars. The juice is at once raised in temperature and a portion of milk of lime is added in order to precipitate the albuminous matters and offer resistance to this tendency to fermentation. The juice is further heated to bring to the surface flaky matters, which are skimmed off. In many Cuban plantations, vacuum pans are employed; in these the juice is evaporated nearly to the crystallizing point. Thus a crude sugar is produced. This crude sugar is exported to the great commercial countries of the world: England, France, Germany, the United States, where the sugar is refined.

In tropical countries the extraction of the sugar from the cane is carried on under considerable difficulties. Hot climates are unfavorable to that untiring industry which characterizes the inhabitants of the great industrial countries of Europe and the United States. Again, high temperature is very injurious to the juice when extracted from the cane: even within an hour from its extraction, fermentation may set in, such as will generate uncrystallizable forms of sugar, or even acetic acid, at the cost of enormous loss of true sucrose. Again, it is found that no amount of mechanical crushing will extract from the cane its full proportion of sweet juice. Its silicious and woody exterior resists the most powerful rollers used for this purpose. Many methods have been attempted with a view of replacing crushers; without much success, however. But the obstacles have been to a considerable extent conquered by the intelligent planter by the application of energy, capital, and scientific knowledge.

In *refining* sugar, there are several distinct stages: 1.—The crude sugar is dissolved in water. 2.—The syrup is carried to the top floor of the refinery, which is usually a very high building. (In subsequent stages, the sugar descends easily from floor to floor.) The syrup, being carried into tanks, is mixed with ox-blood (or even sawdust.) The albumen of the

blood is capable of coagulation by heat ; at the same time, it is very adhesive. The mixture of syrup and blood being heated, and at the same time agitated, the albumen attaches to itself particles of dirt, fibre, mechanical impurities, and to some extent, coloring matters. As the coagulation proceeds, the albumen forms hard lumps which may be easily removed by the next process. (The coagulated albumen, known as blood-waste, is afterwards sold for use in the manufacture of commercial fertilizers. It affords valuable nitrogenous material.)

3.—From the tanks just mentioned, the turbid liquid is strained through cloth bags. A clear syrup passes through, leaving all solid matters on the filters. The clear syrup, however, is somewhat colored.

4.—The syrup afforded by the preceding operation is next carried through filters of bone coal. (Bone coal is manufactured by heating bones in closed iron retorts. The mineral part of the bone is not altered by the operation, but the gelatinous matters — the organic substances diffused through the bone — are decomposed, and they afford a very porous carbon which is very effective in decolorizing liquids.) On passing through the bone coal, the syrup is completely decolorized.

5.—The colorless syrup from the preceding operation is now passed into the vacuum pans. These are immense boilers, so constructed that evaporation may proceed with great rapidity and at comparatively low temperatures. Their effectiveness depends upon the fact that the upper portions of the pan are continually exhausted of air and water vapor by the action of powerful pumps. Thus conditions are afforded whereby water may be vaporized from the syrups without that restraint which would be exerted upon it if air or water vapor were resting upon it. The vacuum pans are ingenious appliances devised and constructed with the highest degree of scientific skill. By their means, the syrup is evaporated to the condition of a saturated solution of sucrose ; and this is accomplished without danger of injury to the sucrose by excessive heat.

6.—From the vacuum pans, the concentrated syrup is drawn out into crystallizing tanks of various kinds. They differ according as the crystals desired are large or small, moist or dry, separate

8

or coherent. Sometimes crystalline loaves are produced, and these by the action of saws are cut up into small cubes. The sawdust in this case is cane sugar. It is pulverized by machinery and thus brought to the condition of powdered sugar.

In all these operations where cane sugar is handled, the greatest care must be taken to avoid fermentation of sucrose into *uncrystallizable* varieties of sugar. In order to accomplish this result, the business is conducted on a very large scale and in such a way that a given portion of sugar is not long in the process; that is, a thousand barrels of raw sugar received to-day are turned out in the form of refined white sugar to-morrow.

Again, iron must be carefully avoided; a small amount of it, such as would not ordinarily be recognized in sugar, would be detected when sugar is used in the sweetening of tea. (Tea contains tannin which at once produces a dark colored compound with iron; the same principle being employed in the manufacture of writing inks.) In order to secure immunity from iron, wooden shovels are employed, and brass and copper vessels of various sorts. Wherever iron apparatus is necessarily involved, it is kept carefully cleaned or protected by paint.

Cane sugar, from the sugar beet. The manufacture of refined cane sugar from the sugar beet has attained enormous proportions in Europe, especially in Germany, France, Russia, and Austria. It has been attempted on a moderate scale in the United States.

The German chemist Marggraf observed in 1747 that beets contain a sugar similar to that of the sugar cane and that it is capable of crystallization. His pupil Achard advanced the practical side of the subject by setting up an experimental works in 1769. Gradually other works were established in Germany. In France, Delessert undertook the manufacture of beet sugar; in 1812, his operations were brought to the attention of Napoleon. The emperor, who was very anxious to encourage domestic industries in France, as opposed to the purchase of goods from foreign nations, ordered the cultivation of an immense tract of country, and appropriated a million francs to further the undertaking. A large number of chemists and manufacturers studied the subject thoroughly, and ultimately the art of making sugar from beets became successful.

It is worth noting that the eminent German chemist Liebig considered the manufacture of beet sugar an unwise one for Germany on the ground that cane sugar could be produced cheaper in tropical climates, whereas the beet sugar of Germany depended on the taxation of a vast body of non-producers in order to

afford it the necessary government support. "The satisfaction of eating sugar grown on our own soil," he says, "is therefore purchased by a not inconsiderable sacrifice." He refers to the fact that the government was paying manufacturers a bonus on beet sugar produced; a state of things, we may add, which up to the present day, continued in one form or another, has given rise to grave questions in Germany. Apparently, to-day, the tax-paying citizens in Germany, the non-manufacturers of sugar, are paying the German sugar manufacturers a certain contribution in order to enable them to furnish beet sugar to the people of England and France at cost. However, the assistance afforded by the Emperor Napoleon and by the German government has developed the beet sugar industry enormously and has brought it to the condition of a very perfect though very complicated manufacture, and, more, inventions and discoveries put in operation in the complex beet sugar industry have been borrowed to great advantage in the simpler operation of producing sugar from the sugar cane.

The following is an outline of the process of manufacture of cane sugar from beets :

(1) Great care is exercised in selecting for cultivation beets of a variety likely to produce the highest yield of sugar; in cultivating these in the most scientific manner so as to develop in them the largest amount of sugar of which they are capable; in harvesting them at the period when the sugar contents are at the highest point.

(2) When harvested, the beets are washed to remove extraneous impurities. They are sliced or rasped and treated with water to extract the sugar. In some cases, Graham's discovery of the high diffusion rate of crystalloids is employed, the juice being placed in *diffusion batteries* so that the largest amount of cane sugar may be absorbed in the smallest amount of water and with the smallest simultaneous absorption of other vegetable matters.

(3) The juice is partly purified by heating to coagulate vegetable albumen and by the addition of lime which assists in this operation. The liquid is then filtered.

(4) The partly purified filtrate is next treated with a large amount of lime — about five per cent. This combines with the sugar, forming an insoluble precipitate, a sort of sucrate. Another filtration separates this sucrate from liquid impurities.

(5) The sucrate of lime is freed from lime by another operation in which carbon dioxide (generated by heating limestone or by burning coke) precipitates the calcium as calcium carbonate, $CaCO_3$, while the sugar is left in solution.

(6)   The syrup is now subjected to a series of processes very similar to those described under the refining of sugar from cane, such as decolorizing the syrups with bone-coal and subsequently crystallizing the sugar by the use of the most perfect mechanical appliances, such as vacuum pans, etc.   Scientific study of a high order has been expended without stint, in order to raise every step to a position of the greatest chemical economy and to advance every mechanical appliance to a condition of the first efficiency.

Cane sugar from sorghum.   The sorghum plant, or Chinese sugar cane, offers some advantage in the manufacture of sugar, in the fact that it flourishes in comparatively cool climates.   Tremendous efforts have been exerted to introduce the manufacture of sorghum sugar into the United States.   Both private individuals and the Department of Agriculture have devoted large sums of money and careful study to the development of this industry,   In some parts of the United States, stimulated by State and National bounties, sorghum plantations and sorghum sugar factories are now in operation.

It seems evident that small farmers cannot undertake the complete business. The sorghum must be grown in a certain favorable belt of country. It must be harvested under careful chemical supervision at exactly that time in the year when its juice has attained its maximum contents of crystallizable sugar with the minimum of those uncrystallizable ones which are a considerable drawback in this industry. The sugar must be extracted from the stalk with the most carefully adjusted diffusion batteries. Subsequently, of course, the juice must be defecated and crystallized by the use of those complex and elaborate combinations of apparatus of which the industries dependent upon the sugar beet and the sugar cane have developed the use.

In brief, the process of the manufacture of sugar from sorghum is as follows :

The cane is first cut into small pieces, about an inch in length.   Next, these pieces are subjected to the action of a fan, whereby the light and comparatively worthless particles are blown away.   The better portions of the cane are then acted upon by a shredding machine which tears the material and gets smaller fragments.   These fragments are submitted to the action of the diffusion battery.   In this apparatus the syrupy juice is extracted. This juice is clarified by the use of lime, after which it is allowed to settle.   Next, the clear juice is partially evaporated into a

tolerably thick syrup. To this syrup, 90 per cent. alcohol is added. By the influence of the alcohol, while the real sugar is dissolved, certain impurities are thrown out in the form of a sediment. The alcoholic syrup being drawn off and distilled, the alcohol is collected for a second use, while a purified syrup remains. This syrup is evaporated in vacuum pans until it is sufficiently condensed for the extraction of solid sugar from it.

The use of alcohol is, in many ways, objectionable, and sorghum sugar may be made without it.

Sugar from the sugar maple. The sugar maple which grows abundantly in the northeastern parts of the United States affords a sugary juice. At the period in early spring when the sap is known to be richest in sugar, the mature trees are tapped ; that is, a small spout is inserted under the bark. The juice, which flows freely, is then quickly boiled down until it is in a condition to harden. A yellowish sugar and a clear and agreeable syrup may be thus secured. As yet, however, no considerable quantities of highly refined white sugar are produced from this source.

Notes on the Synthesis of Sugars.

This important synthesis usually starts with *a*-acrose, a substance that may be produced in at least two ways :

First way.—In aqueous solution, formaldehyde, CH_2O, by action of milk of lime polymerises into a mixture of sugars called formose, $C_6H_{12}O_6$.
From formose, *a*-acrose, $C_6H_{12}O_6$, may be isolated.

Second way.—From glycerol (glycerin), $C_3H_8O_3$, by action of sodium carbonate and bromine, there is produced a kind of sugar called glycerose (a triose) $C_3H_6O_3$.
From glycerose, *a*-acrose may be produced by a spontaneous polymerisation.

Next, starting with *a*-acrose the following briefly described sets of operations lead to the production of certain natural as well as artificial sugars :

First Set.

1.   From *a*-acrose, by addition of phenyl hydrazine, there is produced i-*glucosazone*.

2.   From glucosazone, by action of concentrated hydrochloric acid, there is produced i-*glucosone*.

3.   From glucosone, by action of nascent hydrogen, there is produced i-FRUCTOSE and *i-mannite* (see 4).

Second Set.

4.   From i-mannite, by oxidation there is produced *i-mannose.*

5.   From i-mannose, by oxidation there is produced *i-mannonic acid.*

6.   From i-mannonic acid, by decomposition of the strychnia salt there is produced l-*mannonic* acid (see 7) and d-*mannonic acid* see 9 and 13).

Third Set.

7.   From l-mannonic acid, by quinoline there is produced l-*gluconic acid.*

8.   From l-gluconic acid, by nascent hydrogen there is produced l-GLUCOSE.

Fourth Set.

9.   From d-mannonic acid, by nascent hydrogen there is produced d-*mannose.*

10.   From d-mannose, by phenyl hydrazine there is produced d-*glucosazone.*

11.   From d-glucosazone, by hydrochloric acid there is produced *d-glucosone.*

12.   From d-glucosone, by nascent hydrogen there is produced *d*-LAEVULOSE.

Fifth Set.

13.   From d-mannonic acid, by heating with quinoline, there is produced d-*gluconic acid.*

14.   From d-gluconic acid, by nascent hydrogen there is produced d-GLUCOSE.

NOTE.   Investigators working on the synthesis of sugars, use the symbols d, l, and i, to express respectively series of related compounds rather than distinctively optical properties.   This produces a certain confusion — but it is nnavoidable for the present.

CHAPTER XV.

CARBOHYDRATES (Continued).

Starch.

Distribution. Starch is widely diffused in the vegetable kingdom. It is generally accumulated in seeds as the nutriment of the young sprout, before the latter has become sufficiently developed to draw food from the soil and the atmosphere.

It also exists in roots, tubers, and occasionally in bark and pith. A large proportion of the edible potato is starch. The principal kinds of starch employed as such are wheat starch, corn starch, potato starch, and rice starch.

Starch has not yet been produced artificially.

In preparing corn starch the corn is soaked in water containing a small amount of caustic soda or soda ash. The pasty mass is then placed on screens; the starch washes through; the water and starch being received in suitable tanks, are allowed to rest in quiet until the starch has deposited; thereupon the larger portion of water is drawn away, and the moist starch is dried and made ready for the market. In drying, the mass of starch soon comes to be penetrated by large cracks: thus irregular lumps of starch are left. These must not be considered *crystals*, for they are not such in any sense. On the screens remain the hulls and the germs of the young corn plant. After drying the mass, it is subjected to a process of winnowing; a current of air blows the hulls into one box, while the germs remain in another. From the germs, corn-oil may be produced by pressing. The pomace may be used for feeding cattle.

In preparing potato starch, the potatoes are rasped into a pulp. This pulp is washed in water so as to float off the starch and separate it from coarser matters which remain behind. Subsequently the starch is allowed to subside.

Properties. 1. When examined under the microscope, the starches of different vegetables present different appearances. They are characterized, however, by one general kind of formation; that is, they are formed in eccentric layers, one outside of another. But starches from different sources form granules differing in size and appearance. The granules of potato starch are, generally speaking, the largest; the granules of rice starch are, generally speaking, the smallest; while those of other starches

are intermediate. By the microscope, therefore, different kinds may be distinguished one from another, and mixtures of them may be detected. Of course for completeness of this kind of analysis, reagents like iodine may sometimes be employed to advantage; and polarized light may also be used.

2. To starch is usually assigned the formula $C_6H_{10}O_5$, whatever the source whence it is derived. Whether or not this formula represents correctly the molecule of starch, cannot be at present determined. It is thought that the formula $(C_6H_{10}O_5)_n$ is nearer the truth. It is not certain that the same molecular formula is appropriate to the different kinds of starch.

3. The various starches have certain striking chemical properties in common. Thus, water solutions of iodine turn starch to a deep blue color. The nature of the blue compound is not understood. It does not appear to be a very stable one, since starch blued with iodine loses its color under the influence of heating in water and upon addition of alcohol. Upon the withdrawal of heat or the removal of the alcohol, the blue color reappears.

4. Starch by itself is insoluble in water and all ordinary solvents; but a variety of starch called soluble starch may be produced by boiling starch in water for a considerable length of time. The first action of water upon starch, however, involves merely an opening of the layers in which the granules are formed. The portions constituting these layers being broken off, and floating in the water, give rise to the tenacious mass known as starch paste.

5. Under the influence of certain dilute acids, aided by heat, all kinds of starch change into dextrose or glucose.

Under the influence of strong nitric acid, starch, like other carbohydrates, is capable of forming nitro-compounds, as described under the head of cellulose. These compounds are derivatives in which the nitric acid radicle, NO_3, replaces certain atoms of the hydrogen and, it may be occasionally, of the oxygen of the carbohydrate.

6. When starch is moderately baked it changes to a soluble substance called British gum or dextrin. It is a mixture of carbohydrates of undetermined composition.

7.   Malt extract (by virtue of its diastase) changes starch to dextrin and maltose.

Uses.   1.   In the development of the growing plant, a considerable amount of its energy is devoted to the preparation of the seed.   Here starch, as well as other substances, are stored up. In the process of germination the starch undergoes a fermentation or modification into dextrose, a soluble carbohydrate, which affords nutriment for the young plant.   When this parent supply is exhausted, the more mature plant absorbs food from the soil and atmosphere and then develops a new stock of starch for its successors.

2.   Starch is a prominent factor in the vegetable foods consumed by man and many of the lower animals.   In wheat flour, in corn meal, in oat meal, and in many other important kinds of vegetable food, starch is an important constituent.

When starch acts as a food for man and the higher animals, it undergoes certain changes.   In the operations of cooking, the starch is changed by heat and fermentation into dextrose or glucose, carbohydrates more soluble and digestible than starch. These, acted upon by the juices of the digestive tract, are absorbed into the animal system and contribute to the building up of certain of its materials.   Farinaceous matters contribute to the production of fat as distinguished from muscle, which latter demands nitrogenous food.

3.   Starch is largely consumed in the process of brewing malt liquors.   The starch is fermented into alcohols (p. 70).

4.   Starch is used in making the gummy material sometimes called British gum, sometimes dextrin, which is used as adhesive material on envelopes and postage stamps ; it is also used as a thickening material for mordants used in calico-printing.   In preparing dextrin a small amount of dilute acid is added to starch ; then the mixture is moderately baked in an oven.

5.   Starch is used to produce glucose (p. 109).

6.   Starch is used in starching cotton and linen clothing, and in a similar operation called *finishing* of cotton and linen goods at mills.   It is also used in *sizing* the yarn for warps used in weaving.

CARBOHYDRATES (Continued).

Cellulose.

Distribution. Cellulose, $C_6H_{10}O_5$, is the principal constituent of wood. It is also found in very many other portions of the structure of plants. In the leaves and flowers, in the harder and less soluble parts of seeds, in the peculiar down which constitutes the cotton fibre, cellulose exists.

Cotton cloth that has been thoroughly bleached, has gone through a process which removes resins and waxes from the surface of the fibre, and leaves a substance which is approximately pure cellulose. So old linen that has been washed many times, has been thus freed from many incidental vegetable compounds, and it has been reduced to a form of practically pure cellulose. In the manufacture of wood paper, the wood is macerated in large digesters, whereby gums and resins are partly or wholly dissolved. There is then left the cellular tissue of the wood in fibrous form. (This way of making the wood paper pulp must be distinguished from another method which is employed to produce paper stock. In this second method, the logs of wood are forced against grindstones, whereby the structure of the wood is broken up and what is called *ground wood* is produced.)

The form of cotton used by surgeons and called absorbent cotton, represents a nearly pure form of cellulose. This cotton has been subjected to certain reagents for the express purpose of removing the resin from its surface. It absorbs liquids with much greater readiness than ordinary cotton.

Properties. 1. Cellulose, although a carbohydrate, and in molecular formula supposed to correspond with starch, is in many respects very different from the latter. It is but little affected by water and many chemicals. It is, however, dissolved by a special solution called Schweitzer's reagent. This is an ammonical solu-

tion of cupric oxide. It may be prepared as follows: Dissolve cupric sulphate in water. Then add ammonium chloride. Next, add sodium hydroxide. Pour away the clear liquid, and then add the precipitate to ammonium hydroxide solution. A deep blue solution is produced. This solution has the remarkable property of dissolving cellulose.

2. Cellulose in the form of wood, as portions of trees or portions of buildings, when exposed to the air and moisture, undergoes a peculiar decomposition known as rotting or decay.

3. Hydrocellulose, $C_{12}H_{22}O_{11}$, is formed by the action of certain acids upon cellulose. Thus, strong sulphuric acid or hydrochloric acid accomplishes this change.

Cellulose is acted upon more by acids than by alkalies. Thus, concentrated nitric acid turns it into a nitrate of cellulose called gun-cotton. Chlorine, and the gases evolved by bleaching powder, have a corrosive effect upon cellulose. Bleached cloth, unless thoroughly washed from the chlorine used upon it, often becomes " tender," as the bleachers express it. A small amount of dilute sulphuric acid, placed upon cloth, loses some of its water by evaporation. Thereupon, the stronger acid attacks the cloth and rots it.

This general principle is utilized in the woolen industry. Certain kinds of wool, as coming from the sheep, contain quantities of vegetable seed vessels called burs. These burs are not easily removed by the carding operations. If, however, the burry wool is treated with dilute sulphuric acid and partially dried, the acid attacks the cellulose of the burs without injuring the animal fibre of the wool. If the acid is then washed away and the wool afterwards subjected to the operation of carding, the burs are found to be so much affected by the sulphuric acid that they easily break up into dust and separate from the wool.

A similar process is employed in separating considerable quantities of cotton from wool in old cloths or shoddy which are to be worked over. Sulphuric acid weakens the cotton fibre, so that the subsequent manufacturing operations may save the wool but let the decomposed cotton pass out as dust or waste.

So in the so-called recovery of india-rubber, from old rubber boots and shoes, the material is heated with dilute sulphuric acid which removes the textile fabric from the gum.

Parchment paper. When paper is allowed to rest for a short time in concentrated sulphuric acid and is then thoroughly washed with water, it is found to have undergone a very marked change. It shrinks somewhat and becomes much tougher than before. The substance produced is called parchment paper, and it is largely used as a covering material for the corks of bottles, in substitution for certain animal membranes.

Nitrates of cellulose ; pyroxyline ; gun-cotton. When clean cotton is immersed in nitric acid, or better, in a mixture of nitric acid and sulphuric acid, it changes into a nitrate. The sulphuric acid is used chiefly to withdraw water from the nitric acid and so to strengthen it. The chemical action involves the union of the nitric acid radicle, NO_3, with the cellulose, thereby replacing a certain number of atoms of hydrogen of the cellulose. Several nitrates of cellulose are known, the more explosive ones containing more of the nitric acid radicle.

Thus a *di-nitrate* is known.

The *tri-nitrate* and the *tetra-nitrate* are often formed as a mixture by the same process. When these are subjected to the action of a mixture of ethyl alcohol and ethyl ether they dissolve and produce the substance called *collodion.* If this solution is exposed to the air the solvents evaporate and the gun-cotton is left in the form of a gelatine-like film. This film has been much employed as a coating for glass negatives in photography. It has also been used in certain forms of surgical practice for producing an artificial cuticle upon wounded surfaces.

A *penta-nitrate* has been formed. It is less stable than the others. When a a mixture of tetra-nitrate and penta-nitrate is mixed with alcohol and camphor and the mass is then thoroughly kneaded together the peculiar material called *celluloid* is produced. The hexa-nitrate is avoided because it is explosive, Celluloid burns very quickly but is not explosive.

To cellulose *hexa-nitrate* the formula $C_{12}H_{14}(NO_3)_6O_{10}$ is assigned, will be at once seen to represent two molecules of cellulose, $C_6H_{10}O_5$, in which six atoms of hydrogen have been replaced by six molecules of the nitric acid radicle, NO_3. After the failure of many early attempts to utilize gun-cotton as an explosive, success has at length been attained. At present, most of the great nations of the world manufacture this material for use in torpedoes. It is usually stored in pressed cakes. Indeed, the substance is now considered more safe in use than gunpowder.

Many terrible accidents occurred before the nature of gun-cotton was well understood. Most extensive study of it, however, has shown that such accidents usually arise from gun-cotton which has not been washed perfectly from the acid used in its manufacture.

4. Cellulose is capable of undergoing a kind of limited oxidation by action of bleaching powder solution *with access of air,* whereby a brittle compound called a-oxycellulose is produced. Again, by action of moderately strong nitric acid a variety called b-oxycellulose is produced.

5. *Cellulose not a food.* The fact that living plants, in their processes of growth, produce much larger quantities of the carbohydrate known as cellulose than of the kindred carbohydrate known as starch is worthy of careful consideration. Of course, cellulose is cheaper than starch, pound for pound. Cellulose, however, is not digestible in the animal economy as starch is. In other words, it is not a true food. If chemists could *cheaply* turn

cellulose into starch or into glucose, or into sucrose, the food sup-
ply of the world would be materially enlarged. (A somewhat simi-
lar transformation has been successfully accomplished in the change
of cellulose and starch into glucose. But while the changing of
starch is cheap enough to be practicable, in case of *cellulose* it is
not so, at present.)

Uses. Modern civilized nations use enormous quantities of
cellulose in the manufacture of paper and all the various sub-
stances produced from it ; for example, pasteboard, papier-maché,
etc., and in the manufacture of cotton and linen goods.

Paper.

While ancient peoples of the far East, as the Egyptians
and the Chinese, have long produced considerable quantities
of paper for a multitude of purposes other than for printed books,
for example, for fans, screens, wall decorations, etc., it has been
reserved for Western nations to develop this industry to the
highest pitch. Books and newspapers, paper boxes, wall papers,
paper twine, and many other useful articles, suggest a very few
of the forms in which paper or its equivalents are employed.

In the far East, paper has been made from many vegetable
fibres which were accessible and appropriate for the purpose. In
Europe, the paper manufacture originally employed discarded
cotton or linen goods in the form of rags. At the present time,
while cotton and linen rags are much used for the finest qualities
of paper, the larger proportions of this useful material are made
solely from wood or from mixtures containing large quantities of
wood pulp.

The manufacture of paper from wood may be briefly described
under two heads : first, the caustic soda process (with the soda
recovery process) ; second, the sulphite process.

The caustic soda process. First stage. Different kinds of wood
are used, but poplar is preferred ; inferior kinds of wood, like
spruce, may be employed. The logs of wood are split by a sort
of axe, resembling an enormous chisel, which moves up and down
by machinery. When a log is placed under the axe, the wood is
quickly split into small pieces. Next, the more resinous portions
of the wood are removed by augers, which have both a rotating
motion and an up and down motion, imparted to them from the

engine. A log being placed under the auger, a knot or dark colored portion is quickly drilled out and the wood left clean. Where "slabs" are used, the bark or other dark portions, are shaved off swiftly and economically by a series of blades adjusted spirally on a swift running shaft. The clean wood is then chopped into small fragments, likewise by machine.

Second stage. The chips are boiled in large spherical kettles, called digesters, with a solution of caustic soda (sodium hydroxide). This liquid softens and dissolves the resin, which binds the fibres of the wood together, so that the material soon assumes the form of a thick paste, or pulp. After boiling six or seven hours under the pressure of 120 pounds, a large valve in the digester is opened, and the steam pressure drives the paste out upon screens. Some of the liquid drains away into a tank made to receive it; this liquid is afterwards "recovered" as described later. The pulp, at first as brown as black walnut, is thoroughly washed with water. Next it is bleached by use of a small amount of bleaching powder; it becomes much lighter in color. By passing the pulp through a screen, the water and bleaching powder are removed.

The pulp may then be passed to an ordinary paper making machine and dried into the form of a thick paper. This material is often called pulp in trade; it is a raw material, from which, by finer paper-making machines, the better qualities of marketable paper may be prepared.

The soda recovery. The dark colored liquid that has come away from the soda digesters may be described roughly as containing water, sodium hydroxide, and resinous matters. The latter two may be considered in chemical union, as a sort of resinate of soda. In order to recover the soda for subsequent use, the liquid is subjected to several processes.

First process. The liquid is partly evaporated by some economical system — generally in vacuum pans — the Yaryan process being a favorable one. When evaporation is sufficiently advanced, the liquid is thick and brown, like molasses.

Second process. The thick liquid next flows into a peculiar furnace. This furnace may be described, in general, as composed of three parts. There is a chimney; at about twenty feet from the chimney is a fire-box; set diagonally between the fire-box and the opening in the side of the chimney, is a rotating iron furnace, of cylindrical figure, and completely lined with fire brick. In the fire-box, chips and other waste materials from slabs, etc., used, are burned. They afford a long flame, which sweeps toward the chimney, at the same time

passing through the furnace, whose brick lining becomes intensely heated. Now the molasses-like soda liquid is allowed to flow slowly into the upper end of the furnace. It is evaporated; it is heated red-hot; its carbonaceous matter is partly oxidized; so that after taking a spiral course, it flows out of the lower end of the furnace as red-hot granules. The granules are received in iron buckets; later, they are dissolved, as far as possible, in water. The sodium carbonate, formed in the furnace, dissolves. A black carbonaceous matter, somewhat resembling graphite, remains undissolved.

Third process. The sodium carbonate is causticised by addition of quick-lime. Calcium carbonate is produced as a white precipitate, which is allowed to settle. The clear liquid contains sodium hydroxide, *i. e.*, caustic soda, which is ready for use in the digesters upon a new charge of wood.

The sulphite process. It has been observed that bi-sulphites of calcium and magnesium are very favorable materials for resolving wood into pulp. In what is called the sulphite process, therefore, a bi-sulphite of calcium or a bi-sulphite of magnesium, must be employed.

The apparatus consists essentially of two parts. *The first part* is a series of wooden tanks, placed in the several stories of the building in a descending series. At the bottom of the building is a furnace for burning sulphur. The whole contrivance is air-tight, except as the manufacturer opens valves. The general operation of the apparatus permits a steady stream of liquid, consisting of water and quicklime, or water holding oxide of magnesium in suspension, to flow steadily in at the top of the series of tanks and to be drawn steadily out at the bottom of the series.

While the lime liquid flows downward, the sulphur dioxide flows upward against it: that is, the sulphur, being burned on a hearth at the lower part of the building, forms sulphur dioxide as a gas, which goes through tank after tank, until it reaches the top one. The lime liquid flows downward by gravity; the sulphur dioxide flows upward by pumping; that is, an air-pump connected with the upper tank is continually pumping air or gas through the entire series. As an ultimate result, practically all the sulphur dioxide is absorbed, so as to form bi-sulphite of lime. The system is efficient for several reasons. In the first place, the last portions of the sulphur dioxide, what may be called the weakest portions, are in the highest tank where the lime is strongest. Of course here absorption is most active. Again, the pumps have a tendency to produce a rarification in the tanks. Thus, the tendency is for air to leak into the system, rather than for sulphur

dioxide to leak out, where it would be wasted and where it would cause annoyance to the workmen on the premises.

In the second part, the bi-sulphite of lime, formed as described, is pumped into digesters where chips of wood are placed, and digestion then proceeds in a manner somewhat similar to that already described under the head of the soda process.

The sulphite process is usually applied to poplar wood, so as to produce a higher grade of pulp than that afforded by the soda process ; which latter is applied to spruce and inferior woods. The sulphite pulp is whiter than that produced by the soda process, and is suitable for the manufacture of the higher grades of paper.

Textiles.

Cotton has long been known in the far East.   It was woven into cloth in the times of the Pharaohs.   Mummy cases recently opened have been found to contain cloth which upon examination by the microscope was clearly shown to be made from cotton.   Cotton is still grown in large quantities in Egypt and India. The United States is the great cotton producing country of the world.   The Sea-Island cotton is of long staple and of fine quality.

Cotton as growing, is closely attached to seeds.   The fibre is separated from the seeds by a machine called the cotton gin.   (Within a few years the materials in the seed have been utilized.   The hulls are used for fuel; and the ashes, rich in potassium salts and phosphates, are used as fertilizers.   The kernel is pressed for oil.   The cake, containing some oil, together with starch and vegetable albumenoids, is used as a food for cattle.   The oil expressed is bleached, and much used as a salad oil and in the manufacture of soap.)

When an individual fibre of cotton is examined by the microscope, it presents the appearance of a tube that has been flattened and then twisted into a spiral.   Its tubular structure assists materially in its retaining dye-stuffs applied to it, although some colors adhere only to the surface.   Its spiral condition enables one fibre to attach itself to another fibre, thus enabling the cotton to be spun into fine thread.

If cotton is picked before it is ripe, its fibres are defective and immature and less able to hold coloring matters applied to them.

A considerable portion of the work of cotton machinery has as its aim the placing of the individual fibres in parallel lines. Later, portions of these fibres are twisted so as to produce what

is technically called yarn. The length of an individual fibre is called its staple. Of course, the finer grades of yarn demand a longer staple.

Flax, jute, hemp, and ramie, vegetable fibres largely used for the manufacture of textile products, may be considered as forms of cellulose.

Gums.

There exist in a great many plants certain carbohydrates called gums. They lack crystalline form ; they lack the granular structure exhibited by starch. They are characterized chiefly by the chemical constitution represented by the formula $(C_6H_{10}O_5)_n$; and by a tendency, when treated with water, to swell up and form a gelatinous mass.

Arabin is the name applied to the gum of gum arabic. This substance forms as an exudation upon the bark of trees of the acacia variety. It is obtained chiefly from the interior of Africa through upper Egypt.

Gum arabic is employed in the arts and in medicine. Large quantities are used in the manufacture of mucilage, in the thickening of ink, in the preparation of water colors, and for a few other purposes.

Gelose exists in agar-agar, or Ceylon moss. It is largely used as a thickening in jellies, soups, etc. It is also considerably employed as a medium for the development of microbes in bacteriological experiments.

Bassorin is the special material characterizing gum tragacanth. This substance is remarkable for swelling enormously when placed in water. It forms an excellent paste for certain commercial uses.

Many other plants afford certain varieties of mucilage analagous to gums and belonging to the general class of carbohydrates. Thus, from linseed oil, from quince, from Irish moss, and many other substances, gum-like products are obtained.

Glucosides.

The members of the class of bodies called *glucosides* are widely distributed in vegetable structures (and to some extent in animal structures).

The primary feature of glucosides is this : by certain simple operations they are resolved, by a kind of hydrolysis, into two or more substances, one of which is glucose or some other sugar.

9

Various agencies are capable of accomplishing or aiding the hydrolysis :

1. Heating with water.

2. Heating with water and an acid or an alkali.

3. Action of certain ferments like *emulsin, erythrozym, myrosin*, etc. (Some glucosides exist in the plant associated with certain nitrogenous matters which latter may act as an appropriate ferment in the particular case.)

Glucosides are generally solids ; they are generally rather neutral in reaction ; they are usually extracted from parts of plants by solution in water or dilute alcohol ; most of them consist of carbon, hydrogen and oxygen ; some of them contain nitrogen.

Following is a list of a few important glucosides :

Arbutin, $C_{12}H_{16}O_7$, occurring in arbutus,

Salicin, $C_{13}H_{18}O_7$, occurring in willow bark.

Aesculin, $C_{15}H_{16}O_9$, occurring in bark of horse-chestnut.

Coniferin, $C_{16}H_{22}O_8$, occurring in sap of *coniferæ*.

Ruberythrin, $C_{26}H_{28}O_{14}$, occurring in madder root ; it yields alizarin.

Morindin, $C_{26}H_{28}O_{14}$, occurring as a coloring matter in *morinda tinctoria*.

Quercitrin, $C_{36}H_{38}O_{20}$, occurring in quercitron bark.

Amygdalin, $C_{20}H_{27}NO_{11}$, occurring in bitter almonds.

Indican, $C_{26}H_{31}NO_{17}$, occurring in indigo.

FATTY COMPOUNDS CONTAINING NITROGEN AND SIMILAR NON-METALS.

Amines, Amides, Phosphines, etc.

1.   A very large proportion of the compounds already discussed are capable of forming substitution compounds containing nitrogen.   In some of these the nitrogen atom acts with 3 points of attraction ; in some with 5.

For example :

$$
N \left\{ \begin{array}{l} H \\ H \\ H \end{array} \right. \qquad
N \left\{ \begin{array}{l} CH_3 \\ H \\ H \end{array} \right. \qquad
N \left\{ \begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array} \right. \qquad
N \left\{ \begin{array}{l} H \\ H \\ H \\ H \\ Cl \end{array} \right. \qquad
N \left\{ \begin{array}{l} C_2H_5 \\ H \\ H \\ H \\ I \end{array} \right.
$$

| Ammonia gas | Methylamine | Trimethyla-mine | Ammonium chloride | Ethylammonium iodide |
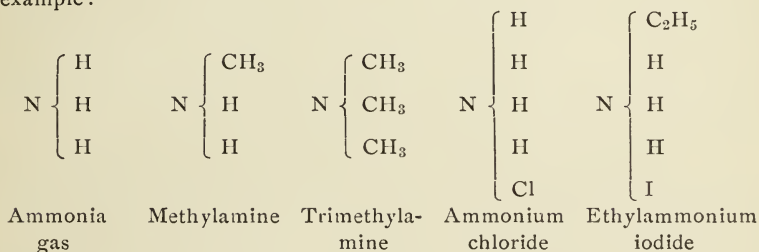
2.   Some, but by no means all, of the nitrogen compounds of the class mentioned, are paralleled by closely corresponding compounds of phosphorus, of arsenic, and of antimony.

For example :

$$
P \left\{ \begin{array}{l} CH_3 \\ H \\ H \end{array} \right. \qquad
As \left\{ \begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array} \right. \qquad
Sb \left\{ \begin{array}{l} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{array} \right.
$$

| Methylphosphine | Trimethylarsine | Triethylstibine |
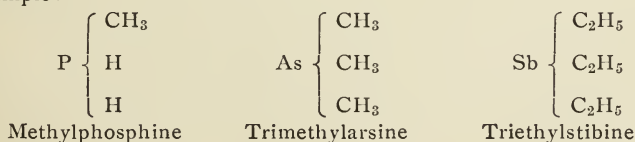
3.   The nitrogen compounds may be regarded from either of two points of view ; *first*, the alkyl, or other similar radicles, may be considered as the passive or type compounds, and then the nitrogen radicle may be considered as the active replacing factor ; *second*, the nitrogenous compound (for example, ammonia gas,

NH_3,) may be considered as the passive or type compound, and then the alkyl radicle, or other carbon compound, may be considered as the active replacing factor.

Thus ethylamine, $C_2H_5 \cdot NH_2$, may be considered as an ethane, in which one atom of hydrogen has been replaced by the radicle amidogen, NH_2; or it may be considered as a kind of ammonia gas, in which one atom of hydrogen has been replaced by the monad radicle ethyl, C_2H_5.

Either view is correct; both should be kept in mind; the one or the other should be chiefly considered, at a given moment, according to convenience. The *second view* is of considerable importance from the fact that compounds are known which represent replacement in ammonium compounds like ammonium chloride, NH_4Cl, and ammonio-platinic chloride $(NH_4)_2PtCl_6$, for example, ethylammonio-platinic chloride, $(NH_3C_2H_5)_2PtCl_6$.

4. In considering nitrogen compounds of the general group under consideration, the student must keep in mind the radicles, ammonium, NH_4, ammonia gas, NH_3, hydrazine, $NH_2 \cdot NH_2$, amidogen, NH_2, imidogen, NH, and finally, nitrogen, N.

Amines. 1. Very many amines are known, but they are more important chemically than industrially. Some exist in natural substances; many are produced artificially.

2. An amine is classed as a mono, di, tri, tetra-amine, according as its molecule is viewed to be derived from one or two or three or four molecules of ammonia gas, respectively.

3. The monamines are classed as primary, secondary, tertiary, according as one, two, or three of the hydrogen atoms of ammonia gas, NH_3, are replaced in the given compound by the alkyl radicle or radicles : thus methylamine, $NH_2(CH_3)$, is a primary monamine ; dimethylamine, $NH(CH_3)_2$, is a secondary monamine ; trimethylamine, $N(CH_3)_3$, is a tertiary monamine.

4. The amines are prepared by various methods. One is by action of an alkyl iodide or similar compound upon ammonia in alcoholic solution. Thus ethylamine may be prepared :

$$C_2H_5I \quad + \quad NH_3 \quad = \quad NH_3C_2H_5I.$$
Ethyl   Ethylammonium
iodide   iodide
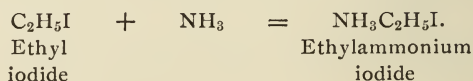
Here the ethylamine in accordance with its similarity to ammonia gas and its general basic character combines with hydriodic acid to form the salt represented, ethylammonium iodide ; but from this

salt ethylamine can be prepared subsequently by distillation with potassium hydroxide (and subsequent purification of the distillate).

5. The amines are generally volatile liquids of alkaline tendency. They generally afford vapors that are combustible.

Methylamine, $NH_2 \cdot CH_3$, dimethylamine, $NH(CH_3)_2$, and trimethylamine, $N(CH_3)_3$, exist in herring brine. They are formed by the decomposition of nitrogenous matters. These amines are also produced with other matters by the dry distillation of certain residual products formed in the beet sugar industry. Here also nitrogenous matters in the beet pulp afford the amines.

Ethylamine, $NH_2 \cdot C_2H_5$. This substance is produced by the putrefaction of certain substances, yeast, for example. It is also formed, together with other products, when the molasses of the beet-sugar manufacture is subjected to dry distillation. It may be produced in the laboratory by a variety of methods.

It is a colorless inflammable liquid, possessing an ammoniacal odor and alkaline reaction. It forms white, smoky fumes with hydrochloric gas as ammonia gas does.

Many other amines are known. The amines produce also a great number of compounds by replacement with chlorine and other halogens, and by combination with other radicles.

Hydrazines and diamines. Amines containing two atoms of hydrogen fall into one of two groups. The *hydrazines* are formed from hydrazine, $NH_2 \cdot NH_2$; in them the two nitrogen atoms are linked; methylhydrazine, $NH_2 \cdot NHCH_3$, is an example. The *diamines*, however, are linked by the carbon atoms; ethylenediamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, is an example.

Amino alcohols. In the molecules of certain alcohols nitrogen or nitrogen radicles may enter. Thus from ethyl alcohol, $CH_3 \cdot CH_2OH$, an aminoethyl alcohol, $NH_2CH_2 \cdot CH_2OH$, may be formed.

Amido acids and acid amides. When a nitrogen radicle is properly introduced by substitution into the molecule of a fatty acid the replacement may occur in at least two ways. Thus if amidogen, NH_2, is to be substituted, it may be introduced either into the *alkyl radicle* of the acid, forming *an amido acid*, or into the carboxyl of the acid, forming an *acid amide*. Thus from acetic acid, $HO \cdot OC \cdot CH_3$, there may be formed amido acetic acid, $HO \cdot OC \cdot CH_2NH_2$, or acetamide, $NH_2 \cdot OC \cdot CH_3$.

In case of certain dibasic acids like carbonic acid and oxalic acid, both amides and amic acids may be formed. Thus:

$$\left.\begin{array}{l} HO \\ HO \end{array}\right\} CO \qquad \left.\begin{array}{l} HO \\ NH_2 \end{array}\right\} CO \qquad \left.\begin{array}{l} NH_2 \\ NH_2 \end{array}\right\} CO$$

<div align="center">

Carbonic   Carbamic   Carbamide

acid   acid   (Urea)

</div>

$$\begin{array}{ccc} HOOC & HOOC & NH_2OC \\ | & | & | \\ HOOC & NH_2OC & NH_2OC \end{array}$$

<div align="center">

Oxalic   Oxamic   Oxamide

acid   acid

</div>
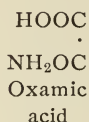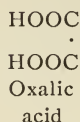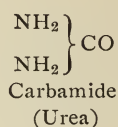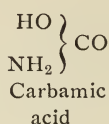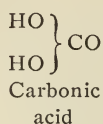
Cyanogen compounds and nitriles. The substance cyanogen, $CN \cdot CN$, and hydrocyanic acid, $H \cdot CN$, and other cyanogen compounds, have been referred to already in another place. But the cyanogen radicle CN may be looked upon as a derivative of methyl, CH_3, the nitrogen atom in cyanogen replacing the three hydrogen atoms in methyl. But cyanogen, being a monad radicle, may be considered as a unit capable of replacing other monad radicles, simple or composite. By such replacement cyanogen may form at least two sets of compounds: the *first*, the *cyanogen acids*, in which cyanogen replaces radicles in the *alkyl part* of an organic acid; the *second*, the *nitriles*, in which the cyanogen replaces the *carboxyl* of an acid. Thus from acetic acid, $HOOC \cdot CH_3$, may be formed cyanoacetic acid, $HOOC \cdot CH_2CN$, also a nitrile, acetonitrile, $NC \cdot CH_3$. (Certain nitriles are alkyl cyanides: acetonitrile is methyl cyanide.)

CHAPTER XVIII.

CERTAIN ORGANIC COMPOUNDS CONTAINING METALLIC ELEMENTS.

A very large number of the compounds already referred to are capable of forming molecules in which metals enter by substitution. The most familiar and evident examples are the acids. These form metallic compounds, of one sort and another, in which the most common are the salts resulting from the replacement of the hydrogen of the carboxyl by one or more atoms of a metal or metals. In most, if not all of such cases, the metal is *indirectly* attached to carbon.

But a considerable number of compounds are known, in which the metal is *directly* united to carbon.

A few examples are given :

$$
\begin{array}{ll}
\text{Bismuth trimethide,} & \text{Bi(CH}_3)_3 \\
\text{Sodium ethide,} & \text{NaC}_2\text{H}_5 \\
\text{Glucinum ethide,} & \text{Be(C}_2\text{H}_5)_2 \\
\text{Magnesium ethide,} & \text{Mg(C}_2\text{H}_5)_2 \\
\text{Zinc propide,} & \text{ZnC}_3\text{H}_7 \\
\text{Cadmium methide,} & \text{Cd(CH}_3)_2 \\
\end{array}
$$

Other compounds, of a similar type or more complex, are known in which enter mercury, aluminium, thallium, germanium, tin, lead, and uranium.

CHAPTER XIX.

AROMATIC COMPOUNDS.

General Statements.

Probably chemists have devoted more study to the aromatic and their allied compounds than to any other group of substances; two chief reasons, the one theoretical and the other practical, may be assigned. The former is the remarkable theory of Kekulé that the molecule of benzene, C_6H_6, has a certain ring-like structure. The latter is the fact that an enormous number of colored compounds suitable for dyeing, the so-called coal-tar colors, may be produced from aromatic hydrocarbons.

Somewhat as the fatty compounds are viewed as derived from marsh gas, methane, CH_4, the aromatic compounds are viewed as derived from benzene, C_6H_6. Aromatic molecules contain the benzene nucleus, C_6, one or more times, and of course in addition other elements.

While a ring formation, based on the benzene nucleus, is characteristic of aromatic compounds, many other ring formations are known: molecules are known having as nuclei 3, or 4, or 5 atoms of carbon. Thus:
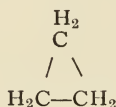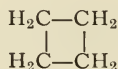
<pre>
          H₂   H₂
          C   H₂C—CH₂   C
         / \ | | / \
     H₂C—CH₂   H₂C—CH₂   H₂C   CH₂
                                                     \ |
                                                    H₂C—CH₂

   Trimethylene   Tetramethylene   Pentamethylene
</pre>
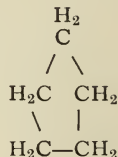
Other ring molecules are known in which, while only carbon is in the nucleus, a different linkage prevails. Again, ring molecules are known in which nitrogen, or oxygen, or sulphur, in one style of linkage or another, exist in the nucleus. Moreover molecules are known in which rings of various sorts are *conjugated*, that is, bound together.

General Characteristics.

First. The aromatic compounds are proportionally richer in carbon than the fatty.

Second. While the fatty compounds readily yield, by decomposition, marsh gas, the aromatic compounds by similar methods of treatment generally yield benzene.

Third. It is comparatively easy to turn one aromatic compound into another, or to turn one fatty compound into another ; but while possible, it is not easy to turn a fatty compound into an aromatic compound or vice versa. When one of these latter kinds of change is made, it involves a deep-seated alteration of structure.

Fourth. In the aromatic hydrocarbons, and their derivatives, it is comparatively easy to replace the hydrogen atoms. Thus such replacement occurs in case of radicles like chlorine, hydroxyl, amidogen, methyl, carboxyl, the nitro group, the sulphonic group. The last two are worthy of particular notice. Nitric acid and sulphuric acid when added to aromatic hydrocarbons, produce respectively, *nitro compounds* and *sulphonic acids*. The same treatment applied to the fatty compounds produces a different class of substances, the esters (in the case of alcohols) ; or else it produces no change.

Fifth. The aromatic compounds have a peculiar kind of isomerism. They produce *ortho*, *meta*, and *para*, and other kinds of isomers ; forms of combinations not recognized in case of the fatty compounds.

Moreover, in certain aromatic compounds, substitution may take place either in the benzene nucleus or in the side chain.

Sixth. When hydroxyl replaces hydrogen of the nucleus of aromatic hydrocarbons there result phenols, substances very different from the alcohols produced by fatty compounds. The phenols manifest acid tendencies, especially when further substitutions of chlorine, bromine, iodine, or the nitro group, or the sulphonic group, occur.

Seventh. In a molecule of benzene, the simplest aromatic compound, and yet more in the higher aromatic hydrocarbons, several radicles may at once replace several hydrogen atoms, and this with comparative ease.

Eighth. While members of the fatty series tend to produce colorless compounds, members of the aromatic series tend to produce colored compounds.

The Benzene Ring.

In accordance with Kekulé's theory which is now very widely received, the constitution of benzene is ordinarily represented as a ring of six carbon atoms, each one attached to its neighbor by one point of attraction on the one side and by two points of attraction on the other. The graphic formula expressed in full is that given in the margin. This method of representing the substance has been objected to by some chemists, and two or three other systems have been devised.
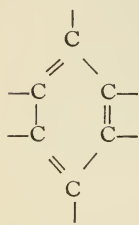
Some chemists prefer Ladenburg's method which represents benzene as a triangular prism, the carbon atoms being placed respectively at the six solid angles.

Von Baeyer's view is preferred by many. This view is approximately expressed by the adjacent diagram for benzene (which accords with facts as well as the other diagrams).

Von Baeyer's theory accords well with the view, now widely held, that the points of attraction of a carbon atom exist in space as if at the apexes of a tetrahedron. If six such tetrahedrons are allowed to stand compactly on a table, there appear six summits at which six hydrogen atoms may be attached (C_6H_6).

Grounds for Acceptance of Kekule's or Some Similar Formula for Benzene.

The structural formula devised by Kekulé for benzene is now generally adopted. While it is open to certain theoretical objections, it has proved highly useful in practice. The following propositions with respect to the benzene molecule are discussed upon the temporary assumption that Kekulé's formula is true; but many of the facts (and inferences) apply with equal force to the other structural formulas proposed:

First. The empirical formula of benzene is C_6H_6. Quantitative analysis shows that the carbon and hydrogen in the molecule bear to each other the relations required by this formula.

The vapor density of the substance leads to the adoption of this formula as against the double, treble, or any other higher multiple of it.

Second. In the benzene molecule C_6H_6, at least some of the bonds of attraction between the adjacent carbon atoms are greater in number than one; for admitting that the carbon atoms in the benzene molecule assume the form of a ring, if all of these carbon atoms were attached to neighboring atoms by only one point of attraction, the hydrocarbon would require the formula C_6H_{12}. (Such a benzene derivative has indeed been practically realized, so has a somewhat equivalent compound, $C_6H_6Cl_6$, produced from benzene. But this may be called an *addition* compound as distinguished from a *substitution* compound.) Now substitution compounds like C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, $C_6H_2Cl_4$, C_6HCl_5, and C_6Cl_6, have been produced.

Many other such substitution compounds are well known : compounds formed on the type of those just enumerated, only having radicles other than Cl substituted for H.

Since, then, an atom of carbon is admitted (on the basis of facts not here stated) to have four points of attraction, it is evident that in the benzene ring some of the atoms of carbon are attached to other atoms by more than one point.

Third. The atoms of carbon in the benzene ring are of equal value and chemical force.

When one atom of chlorine is made to replace one atom of hydrogen by proper chemical operations, the compound monochlorbenzene, C_6H_5Cl, is produced. The composition of this substance has been learned by quantitative analysis. Many times and by many different methods the substance having the formula stated has been made. All these *different portions* of this particular compound or substance are alike. Up to the present time, therefore, *but one kind of compound* having the composition C_6H_5Cl, has been produced. This sustains the proposition just stated, since it may be assumed that in different times of the manufacture of the substance in question, different atoms of carbon in a given molecule of benzene have had one atom of hydrogen replaced by one atom of chlorine.

In these cases if the different atoms of carbon of the benzene molecule had different chemical power or relations, different isomers of the substance named would have been obtained; but no such isomers have been obtained.

The same line of argument may be employed with other compounds of a similar general nature, for example, compounds in which one atom of bromine, one atom of iodine, one molecule of hydroxyl, one molecule of the nitro group, one molecule of the sulphonic group, and of others, have been used to replace one atom of hydrogen in a molecule of benzene. In no case, however, *in such single replacements* have isomers been obtained.

These additional facts further sustain the opinion that the carbon atoms of the benzene molecule have all the same chemical quality and character.

These facts seem further to prove that what may be called the *extra* points of attraction of the carbon atoms are evenly distributed throughout the ring.

Then the proper distribution of the extra points of attraction will be symmetrical.

In accounting for the formation of the compound $C_6H_6Cl_6$, it may be assumed that one point of attraction swings out from each carbon atom to attach an extra atom of chlorine to the molecule.

Fourth. In the general cases of compounds, where more than one atom of an element, or molecule of a radicle, is substituted for hydrogen, substances of the following types may be considered :

    (a)   Compounds of the general formula $C_6H_4A_2$.
    (b)   Compounds of the general formula $C_6H_3A_3$.
    (c)   Compounds of the general formula $C_6H_3AB_2$.
    (d)   Compounds of the general formula C_6H_3ABC.

(a) Disubstitution products. Compounds of the general formula $C_6H_4A_2$. Of these, in a given case, three isomers have been recognized.

(b) Trisubstitution products. Compounds of the general formula $C_6H_3A_3$. Of these, in a given case, three isomers have been recognized.

Compounds of the general formula $C_6H_3AB_2$. Of these, in a given case, six isomers are possible.

Compounds of the general formula C_3H_3ABC. Of these, in a given case, ten isomers are possible.

(c) Tetrasubstitution products. Compounds of the general formula $C_6H_2A_4$. Of these, in a given case, three isomers have been recognized.

Compounds of the general formula $C_6H_2AB_3$. Of these, in a given case, seven isomers are possible.

Compounds of the general formula $C_6H_2A_2B_2$. Of these, in a given case, thirteen isomers are possible.

Compounds of the general formula $C_6H_2ABC_2$. Of these, in a given case, sixteen isomers are possible.

Compounds of the general formula C_6H_2ABCD. Of these, in a given case, thirty isomers are possible.

(d) Pentasubstitution products. Compounds of the general formula C_6HA_5. Of these, in a given case, only one compound has been recognized.

Hexasubstitution products. Compounds of the general formula C_6A_6. Of these, in a given case, only one compound has been recognized.

Orientation in the Benzene Series.

This title refers to the assumed position in the benzene ring at which combination ensues in the case of an element or radicle substituted for a part of the hydrogen of benzene.

The actual existence of a great number of the numerous possible isomers just referred to leads of necessity to the conclusion that they owe their peculiar differences to special *relative positions* (not absolute ones) held by the substituting radicles. In order to describe the relative positions in the benzene molecule a definite notation has been adopted. It is customary to number the carbon atoms from one to six, commencing at the topmost and proceeding round in the direction of clock hands. The designations of the several atoms are indicated by the diagram.

Monosubstitution products. It has already been proved that in *monosubstitution products* a single atom, substituted for hydrogen in the benzene molecule, may take equally well any position on the ring.

Disubstitution products. It is assumed that the atoms of the substituting element may occupy the positions :

> 1, 2, or 1, 6, called ortho, or o.
> 1, 3, or 1, 5, called meta, or m.
> 1, 4,   called para, or p.

The assumption has in this case been borne out by the facts as already stated. Indeed the preceding proposition as to the quality and the chemical force of the carbon atoms in the benzene molecule is supported by the results in the case of disubstitution compounds.

Trisubstitution products. Substituting elements or radicles may have the positions :

> 1, 2, 3, called consecutive.
> 1, 3, 5, called symmetrical.
> 1, 2, 4, called irregular.

Tetrasubstitution products. Substituting elements or radicles may have the positions :

> 1, 2, 3, 4, called consecutive.
> 1, 2, 4, 5, called symmetrical.
> 1, 2, 3, 5, called irregular.

Pentasubstitution products and *hexasubstitution products* will be seen to fall into some of the earlier cases, or else to be too compli-

cated for further discussion here.   However this may be, they are *capable* of discussion in accordance with the numbering system adopted.

A Few Examples.

Reference has already been made to the actual existence of three isomers in case of disubstitution compounds like dibrombenzene ; and the differences have been shown to be dependent upon the *relative* positions of the bromine atoms.   The following diagrams represent the assumed positions :

| 1, 2, Ortho, o. | 1, 3, Meta, m. | 1, 4 Para, p. |
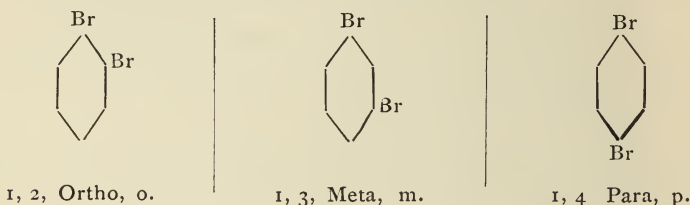
Now the truth or falsity of the theory represented by the foregoing diagrams may be estimated by introducing, for example, more bromine or molecules of some other radicle than bromine. First, upon addition of more of the same element, in this case, bromine, the ortho compound, is capable of producing two isomeric tribrombenzenes ; the meta compound can afford three isomeric tribrombenzenes ; the para compound can yield only one tribrombenzene.   This state of things may be more clearly presented by the following diagrams :

Two tribrombenzenes producible from ortho-dibrombenzene	Three tribrombenzenes producible from meta-dibrombenzene	One tribrombenzene producible from para-dibrombenzene
1, 2, 3. 1, 2, 4.	1, 2, 3. 1, 2, 4. 1, 3, 5. (1, 3, 4.)	1, 2, 4.
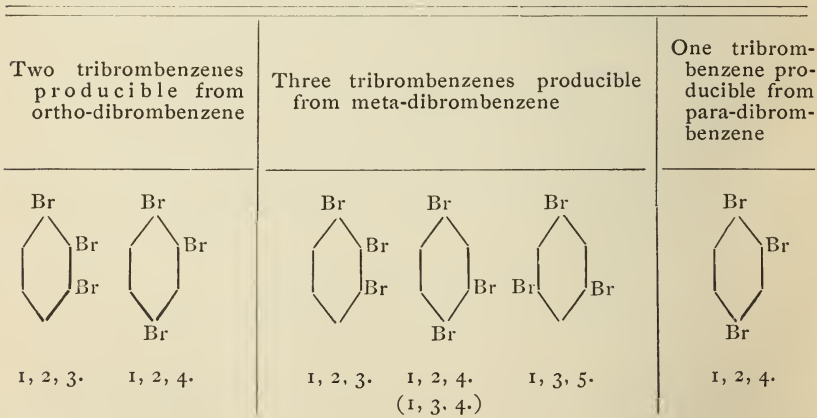
Only three *different* compounds are represented above.

The argument acquires greater force when in dibrombenzene the group NO_2, called nitroxyl, is added. The different dibrombenzenes are by this means able to afford only two isomers for the ortho form, three isomers for the meta form, and one compound for the para form. These results may be made more apparent by a consideration of the following diagrams (all for dibromnitrobenzene) :

| 1, 2, 3. | 1, 2, 4. | 1, 3, 2. | 1, 3, 4. | 1, 3, 5. | 1, 4, 2. |
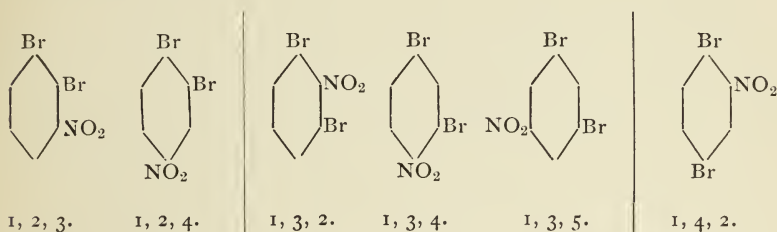
A vast number of other benzene derivatives have been studied in a similar fashion, and the facts obtained have afforded a sufficient basis for the adoption of Kekulé's or some similar diagram for benzene and also for the acceptance of the views as to the ortho, meta, and para positions heretofore referred to, Moreover the substitution compounds of *hydrocarbons other than benzene* have been subjected to a similar kind of study, and from them isomers, showing equally pronounced influence of *relative position in the molecule*, have been produced.

Again, when a given di-isomer is under investigation the question whether it is an ortho, a meta, or a para compound, is settled when it is discovered by experiment whether it can produce two or three, or only one tri-isomer respectively.

Sources of Aromatic Hydrocarbons.

1. Some of them are found in petroleum, especially the Caucasian and the Galician.

2. In a few cases they exist ready-formed in plants.

3. They may be produced by destructive distillation of wood or of resin. The great source is the distillation of cannel coal in the manufacture of illuminating gas. The coal-tar and the various naphthas of this industry contain an immense number of hydrocarbons as well as of other organic substances.

Berthelot has observed a most interesting fact ; namely, that benzene may be produced by a consolidation of acetylene molecules. Thus :

$$3C_2H_2 = C_6H_6$$
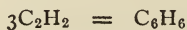
Another method of presenting this phenomenon is that given by Roscoe and Schorlemmer, as follows :
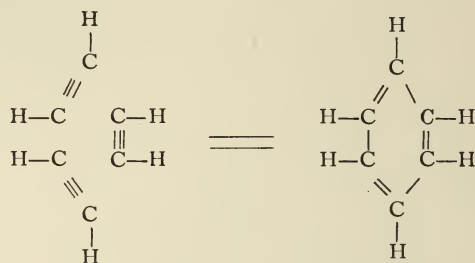
Still other aromatic hydrocarbons have been produced in a similar way : indeed, in many cases, by passing vapors of the lower hydrocarbons through red-hot tubes, higher hydrocarbons may be produced. It is believed that the higher hydrocarbons found in coal-tar are formed from the lower by this sort of molecular consolidation.

4. Special aromatic hydrocarbons may be produced by definite chemical reactions. Thus :

C_6H_5Br	+	CH_3I	+	$2Na$	=	$C_6H_5CH_3$	+	$NaBr$	+	NaI
Monobrom- benzene		Methyl iodide		Metallic sodium		Methyl benzene		Sodium bromide		Sodium iodide
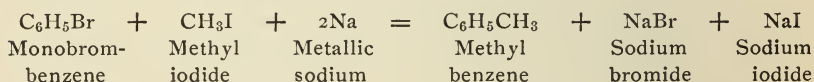
HYDROCARBONS OF THE AROMATIC SERIES.

The hydrocarbons of the aromatic group form several separate series, each series having a general formula of similar type to those already assigned for the hydrocarbons of the fatty group. Each series may have many members.

Series Formula	First Member	Special Formula
$C_n H_{2n}$	Hexahydrobenzene,	$C_2 H_{12}$
$C_n H_{2n-2}$	Tetrahydrotoluene,	$C_7 H_{12}$
$C_n H_{2n-4}$	Dihydrobenzene,	$C_6 H_8$
$C_n H_{2n-6}$	Benzene,	$C_6 H_6$
$C_n H_{2n-8}$	Phenylene,	$C_6 H_4$
$C_n H_{2n-10}$	Phenylacetylene,	$C_8 H_6$
$C_n H_{2n-12}$	Naphthalene,	$C_{10} H_8$
$C_n H_{2n-14}$	Biphenyl,	$C_{12} H_{10}$
$C_n H_{2n-16}$	Acenaphthalene,	$C_{12} H_8$
$C_n H_{2n-18}$	Anthracene,	$C_{14} H_{10}$
$C_n H_{2n-20}$	Fluoranthrene,	$C_{15} H_{10}$
$C_n H_{2n-22}$	Pyrene,	$C_{16} H_{10}$
$C_n H_{2n-24}$	Chrysene,	$C_{18} H_{12}$
$C_n H_{2n-26}$	Phenylanthracene,	$C_{20} H_{14}$
$C_n H_{2n-28}$	Dinaphthylethylene,	$C_{22} H_{16}$
$C_n H_{2n-30}$	Dinaphthylacetylene,	$C_{22} H_{14}$
$C_n H_{2n-32}$	Dinaphthylanthrylene,	$C_{22} H_{12}$
$C_n H_{2n-34}$	Dinaphthyldiacetylene,	$C_{24} H_{14}$
$C_n H_{2n-36}$	Dibiphenylene-ethene,	$C_{26} H_{16}$
$C_n H_{2n-38}$		$C_{26} H_{14}$
$C_n H_{2n-40}$	Carbopetrocene,	$C_{24} H_8$

Hydrocarbons of the Benzene Series, $C_n H_{2n-6}$.

Above one hundred hydrocarbons, of this special series, are known.   A few are mentioned below :

Benzene,	C_6H_6		
Toluene,	C_7H_8	$C_6H_5 \cdot CH_3$	
Ethylbenzene,	C_8H_{10}	$C_6H_5 \cdot C_2H_5$	
Xylene,		$C_6H_4(CH_3)_2$	
Propylbenzene,	C_9H_{12}	$C_6H_5 \cdot C_3H_7$	
Cumene,		$C_6H_5 \cdot CH(CH_3)_2$	$\left\{ \begin{array}{l} 8\ \text{comps.} \\ \text{known.} \end{array} \right.$
Mesitylene,		$C_6H_3(CH_3)_3$	
Normal butyl benzene,	$C_{10}H_{14}$	$C_6H_5 \cdot C_4H_9$	$\left\{ \begin{array}{l} 24\ \text{comps.} \\ \text{known.} \end{array} \right.$
Cymene,		$CH_3 \cdot C_6H_4 \cdot CH(CH_3)_2$	
Normal amylbenzene,	$C_{11}H_{16}$	$C_6H_5 \cdot C_5H_{11}$	(21 known)
Many others, up to	$C_{25}H_{44}$	————	

1.   A mere inspection of the above list shows that many isomers are possible.

2.   Several of the compounds mentioned contain molecules in which an aromatic group and a fatty group are united.   This is significant.   In substitution compounds from such molecules, if replacement occurs in the benzene nucleus, then the compound formed shows aromatic relationships ; but if replacement occurs in the fatty side-chain, the compound formed has properties of a fatty character.

3.   Many of these compounds are found in coal tar.   Many of them are producible artificially.

Benzene, C_6H_6.   Benzene occurs in small quantities in nature in certain petroleums, especially those of Burma and Galicia.

It is produced artificially by the destructive distillation of cannel coal, of wood, and of many other organic substances.

Reference has already been made to its production by the heating of certain other hydrocarbons, even those of the fatty groups, for example its synthetic production from acetylene, C_2H_2.

The supply of the substance for commerce is mainly from the coal-tar produced in the manufacture of illuminating gas.   This tar collects in certain of the condensers and wells, and is afterwards separated.   It contains apparently hundreds of different substances; only a few of them, however, are as yet of

importance. From it are carefully separated benzene, toluene, anthracene, and a few others.

For the separation of benzene, the coal-tar is introduced into enormous iron retorts or stills. The contents of the retorts being heated, a rough fractional distillation is accomplished. The fractions obtained are of three or four different grades. That called " first runnings " contains considerable benzene mixed, however, with other substances. The next portion collected is called "light oil," or " crude naphtha." Another portion, later collected, is called " middle oil." Another portion, later collected, is called " heavy oil," or " dead oil." This portion is often separated into two portions, the one called creasote oil and the other anthracene oil. Finally, there is left in the retort a heavy mass (having a high boiling point) called pitch.

The second fraction called " light oil," is the portion from which the different kinds of benzene are obtained. This oil is subjected to a more careful fractional distillation and thus made to afford benzene, somewhat impure, but of better quality than that originally obtained. It also furnishes toluene and several other hydrocarbons.

At ordinary temperatures benzene is a colorless liquid possessing a characteristic odor. It burns with a luminous but smoky flame. It is distinctly poisonous. Notwithstanding its large number of carbon atoms it has a relatively stable molecule. Yet it easily undergoes a very large number of chemical changes whereby one or several of the hydrogen atoms in the molecule are replaced by other radicals.

Its chief use in the arts is in the production of nitro-benzene and thence aniline and the various aniline colors.

Toluene, or methyl benzene, C_7H_8, or $C_6H_5CH_3$. This is the second member of the benzene series, and it is often found associated with benzene in operations leading toward the production of the latter. Thus, it is produced by the distillation of resin, especially that contained in balsam of Tolu. This latter substance is obtained in the district of Tolu in the neighborhood of Cartagena in New Granada, South America. The balsam is obtained by means of incisions in the trunk of a large tree, *myrospermum toluiferum.* The juice which exudes hardens into reddish brown masses.

Toluene is ordinarily obtained from the oils of coal tar which contain benzene. The benzene and toluene are separated by fractional distillation as already stated in another place.

Toluene is a liquid somewhat resembling benzene. Like the latter substance, it is capable of forming a very large number of

compounds, many of which have been carefully studied. Thus, it forms various chlorine and bromine substitution compounds. It also forms important nitro compounds.

The following series of hydrocarbons is interesting. It suggests, however, a large number of other compounds producible, in similar fashion, *by further replacement or different positions of the same or different fatty radicles in a single benzene nucleus or even in other hydrocarbons having more than one benzene nucleus in the molecule.*

o-Xylene,

$$\begin{array}{c} H \\ HCH \\ \diagup\diagdown\ \backslash H \\ CH \\ H \end{array}$$

m-Xylene,

p-Xylene,

1-2-3 Cumene,

1-3-5 Mesitylene,

1-2-3-4 Cymene, (durene)
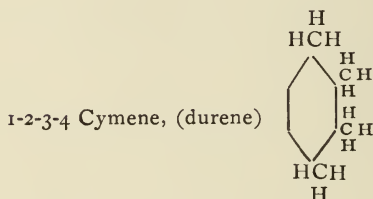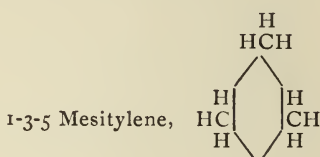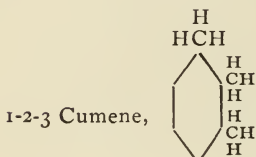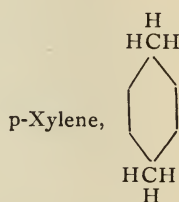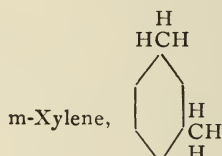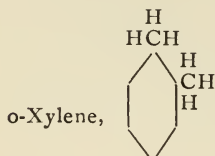
Hydrocarbons of the formula $C_{12}H_{18}$. (14 compounds known.) The substance mellitene, which is hexmethylbenzene, has the rational formula $C_6(CH_3)_6$. This formula itself is a very simple and interesting illustration of the power of substitution of the organic radicle methyl. The formula really represents a molecule of benzene, C_6H_6, in which every atom of hydrogen has been replaced by the radicle methyl, CH_3. The substance itself has been produced by a variety of chemical operations; among others, by the reaction of certain chemical compounds, including methyl compounds and benzene.

Hydrocarbons of the Naphthalene Series, $C_n H_{2n-12}$.

About twenty hydrocarbons of this series are known. The most important is naphthalene.

Naphthalene, $C_{10}H_8$. This substance, at ordinary temperatures, is a white crystalline solid. It is produced in considerable quantities by the distillation of cannel coal in the manufacture of illuminating gas. It has long been a source of great annoyance to gas manufacturers. Occasionally, for some unexplained reason, the naphthalene has been able to pass all the various condensers of the gas works and find its way in considerable quantities into the distribution pipes. There it has sometimes condensed in such amounts as to clog the pipes and seriously interfere with the distribution of the gas.

It is formed in many cases where organic substances are subjected to destructive distillation, especially when the vapors so produced are highly heated as they pass through tubes.
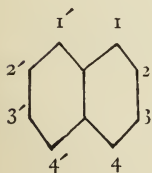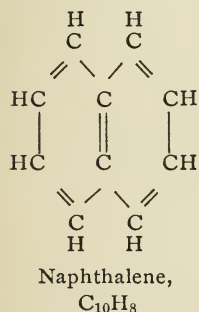
The naphthalene molecule is believed to represent a consolidation of two benzene nuclei, as represented in the upper diagram in the margin. But it is usually represented in the abridged form given in the lower diagram (only without the numbers).

The numerous isomers of naphthalene derivatives have been carefully studied. As a result, the following view has been formulated: when a single radicle, R, is substituted for hydrogen in naphthalene, it may form one of two compounds, according to its position on the ring; if it occupies either of the positions, 1, 1', 4, 4' it produces what is called an *alpha* compound (often designated by a prefixed to the name); if it occupies either of the positions 2, 2', 3, 3', it produces what is called a *beta* compound (often designated by β prefixed to the name.)

(Several notations, other than that indicated by the numbering shown on the margin, have been suggested; it is thought that the numbering here employed has distinct advantages.)
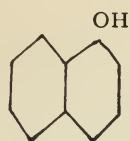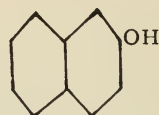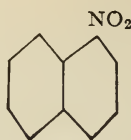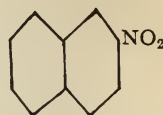
a-naphthol β-naphthol a-nitronaphthalene β-nitronaphthalene

Hydrocarbons of the Anthracene Series, $C_n H_{2n-18}$.

About thirty-two hydrocarbons of this series are known. The most important is anthracene.

Anthracene, $C_{14}H_{10}$. This hydrocarbon was long ago recognized as a constituent of coal-tar. It was formerly considered as a worthless substance, being used as a lubricant under the name of *green grease*. But Graebe and Liebermann showed that alizarin, the chief dyeing material in madder, might by reducing processes yield anthracene. Thereupon they perceived that if alizarin could yield anthracene, anthracene might be turned into alizarin. They succeeded in accomplishing the desired achievement. The process of manufacturing alizarin from anthracene has since been cheapened so that artificial alizarin is now largely used in dyeing and calico printing.

The structural formula of anthracene may be considered as that of ethane, in which two pairs of hydrogen atoms have been replaced by two benzene rings.
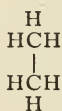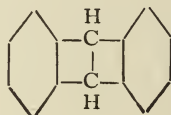
Ethane, C_2H_6 Anthracene, $C_{14}H_{10}$

The importance of the manufacture of artificial alizarin has led to the careful collection of the largest possible amount of anthracene from coal-tar.

Anthracene when pure is a white solid, forming glistening, crystalline scales. It does not dissolve in water. It dissolves in certain organic liquids, like alcohol, ether, chloroform, carbon disulphide, light petroleum, hydrocarbons, etc. It dissolves in much larger quantity in toluene.

Anthracene forms an insoluble red picrate, with alcoholic solution of picric acid.

Oxidizing agents turn anthracene in anthraquinone.

Sulphuric acid produces sulphonic acids.

CHAPTER XXI.

CERTAIN SPECIAL AROMATIC HYDROCARBONS.

Terpenes, Etc.

A number of hydrocarbons having the common formula $C_{10}H_{16}$, or some multiple of it, have been recognized. They find their chief representatives in certain constituents of turpentine, in certain etherial oils such as oil of lemons (and oils of other odoriferous vegetable matters) substances having the formula $C_{10}H_{16}$, or some multiple of it. These hydrocarbons are closely related to camphor and also to gutta percha and caoutchouc (India rubber.)

Terpenes. The vegetable substances analogous to turpentine appear to contain a number of different substances. These are thought to be represented by the following groups:

1st Group.	*2d Group.*	*3d Group.*
Pinene,	Limonene,	Terpinene,
Camphene.	Dipentene,	Phellandrene.
	Sylvestrene,	
	Terpinolene.	

While the formulas of these substances have not been well made out, the following may be presented:

Camphene,
$C_{10}H_{16}$

Pinene,
$C_{10}H_{16}$
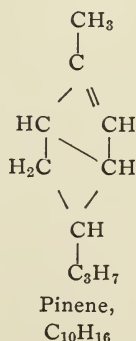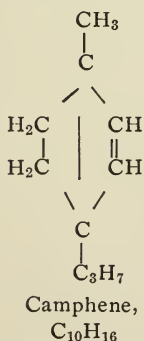
Oil of Turpentine. This substance is largely produced in the United States, especially in North Carolina, from the pine tree of that region, *pinus australis.* Oil of turpentine as found in commerce is a composite substance containing not only hydrocarbons but certain oxidation products. The substance has a considerable affinity for oxygen, absorbing the latter from the air and thus becoming thick and gummy. The action of chlorine gas upon oil of turpentine is well known. At ordinary temperatures the two substances react, the chlorine combining with hydrogen and producing flame, while large quantities of the carbon escape in the form of a black smoke. Incidentally, however, chlorine combines with the radicles present, producing chlorine substitution compounds.

Turpentine. The turpentine industry of the United States is practically confined to a belt of about one hundred miles in width along the Atlantic and Gulf coasts, from North Carolina to Louisiana. The importance of the industry may be recognized from the considerable annual value of the product, nearly $10,000,000. But the influence this industry exerts on the condition of the forests involved must not be overlooked. The securing of so-called *naval stores*, this term including all the resinous products and their derivatives gathered from coniferous trees, has been conducted in a very wasteful and careless manner. Indeed, considering the crude methods employed and the disastrous incidental conflagrations, which destroy vast areas of valuable timber, this industry has been declared to be one of the most unprofitable, all things considered, carried on by this country.

The name employed, naval stores, is due to the fact that the largest consumption of these products is referable to ship construction and ship management. Of course the increasing use of iron in ship-building tends to release a some what increasing proportion of naval stores for other industries.

In securing turpentine from the tree different methods are employed. In some cases a scar or other incision is formed upon the tree. The liquid may flow into vessels or may dry in the form of resinous lumps upon surfaces. In other cases bore-holes are made and the resinous material may be collected in the heart of the wood. It is said that a prejudice has long existed against timber obtained from trees that have been tapped or bled. Recent thorough investigations have shown that this prejudice is not justified by facts.

The chief products of the turpentine industry are the following:

First. Resin or crude turpentine. This is the crude material obtained by tapping or bleeding the trees. It is a mixture of resinous material and oil of turpentine, the latter holding the resins partly in solution, partly in suspension. The material varies very much in quality; in some cases being liquid, in others semi-liquid or solid. In color these original resins vary from yellow to dark brown. Even the more liquid ones harden on exposure to the air.

Second. Spirits of turpentine, or oil of turpentine. This is a liquid distillate from the crude resin. When pure it is a mixture of hydrocarbons of the gen-

eral formula $C_{10}H_{16}$. The impure product, as obtained from the still, contains however other hydrocarbons and acids. By further distillation a purer spirit of turpentine may be obtained. This product is used in the arts mainly for the preparation of varnishes and paints, and in the rubber industry. It has had considerable use in the preparation of an illuminating oil—the liquid material formerly well known under the name of *camphene.* Spirit of turpentine has also wide use in certain medicinal preparations.

Third. Rosin, or colophony. When crude turpentine is distilled for the production of spirit of turpentine, a residue is left in the retort. This residue hardens upon the cooling incidental to withdrawal. It may be transparent or almost opaque. It may be pale yellow or deeper shades, almost to black. Sometimes it is tolerably soft, sometimes very hard. This rosin is used in the manufacture of varnish, sealing-wax, putty, soap, paper, in certain bleaching operations, and for the preparation of subordinate products.

When rosin is submitted to dry distillation, at least three products are obtained.

The first product, called light rosin oil, is used in the manufacture of varnishes.

The second product, called heavy rosin oil, is used in the manufacture of printers' ink, machine oil, axle grease, etc.

The third product is called common pitch. It is a glossy, black, brittle substance. It is used in a variety of forms for waterproofing purposes.

Fourth. Brewers' pitch. This substance is obtained when crude turpentine is distilled incompletely; that is, before the oil has all been expelled. This oil of turpentine remaining gives the brewers' pitch certain desirable qualities; enables it, for example, to adhere to a surface to which it is applied. The best quality of this product is obtained from the larch and is produced mostly in the Tyrol.

Brewers' pitch is used for smearing the inner surface of beer kegs.

Fifth. Tar. This substance is not exactly a by-product of the turpentine orchard. On the contrary, it is a product of destructive distillation of a wood juice. Commercial tar is still and has been for a long time chiefly produced in North Carolina. Certain portions of perfectly dry wood are cut into suitable billets, then piled into a conical stack in a circular pit lined with clay. The pile is covered with sod and earth and at length is fired by means of passages or apertures at the base. A slow, smoldering combustion is maintained. After the ninth or tenth day the flow of tar begins and continues for several weeks. The tar is dipped from the pit and transferred to barrels.

Sixth. Oil of tar. This is obtained by distillation of the tar. It is a complex mixture containing hydrocarbons, some wood alcohol, a small quantity of creosote, certain empyreumatic substances. It is used both as an insecticide and in certain crude forms of medical practice.

Camphor, $C_{10}H_{16}O$. This valuable resin is obtained in Formosa from the camphor tree, *laurus camphora,* which grows in many regions in the Orient. The camphor is obtained from the tree by a very coarse and wasteful method. The wood being cut into suit-

able billets is subjected to the action of heat and steam in such a way that the camphor is expelled and afterwards collected in earthen jars. Subsequently, the raw camphor is subjected to more careful distillation in order to produce the white material commonly seen in civilized countries.

Different structural formulas have been proposed for camphor. The following is the result of recent studies :

$$
\begin{array}{ccccc}
\text{H} & & \text{H} & & \text{H} \\
\text{HC} & \!\!-\!\!-\!\! & \text{C} & \!\!-\!\!-\!\! & \text{CH} \\
| & \text{H} & | & \text{H} & | \\
| & \text{HC} & \!-\! \text{C} & \!-\! \text{CH} & | \\
| & \text{H} & | & \text{H} & | \\
\text{HC} & \!\!-\!\!-\!\! & \text{C} & \!\!-\!\!-\!\! & \text{CO} \\
\text{H} & & | & & \\
& & \text{HCH} & & \\
& & \text{H} & &
\end{array}
$$
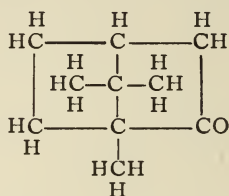
Camphor volatilizes at ordinary temperatures. A small amount placed at the bottom of a bottle will in time transfer itself by volatilization and condensation to the upper part of the same vessel. Its pungent odor is another evidence of its volatilizing.

A curious and well-known experiment is now believed to be dependent upon this same tendency to volatilize; namely, when fragments of camphor are thrown upon clean water, they at once set up a very active rotation upon the surface of the liquid. If a needle or glass rod or other substance having a very minute amount of oil upon it, is plunged into the upper layers of the water, the rotation of the gum instantly ceases. It is believed that the rotation is due to the rapid vaporization of the camphor upon certain sides, and that the vapor pressure produces a reaction which leads the granules to rotate in a contrary-wise direction. It is supposed that the oil spreads in a thin film over the fragments of the camphor and thus prevents evaporation.

Caoutchouc, or India rubber, $(C_{10}H_{16})_n$. It has long been the custom of natives of certain parts of South America to obtain the gum called caoutchouc from certain native trees. The method employed in general has been to perforate the bark of the tree and then collect in a convenient vessel the milky juice which flows freely. Into this juice the natives dip some sort of wooden mold. When the mold is coated with a thin film, the latter is heated over an ordinary fire. The film soon hardens, and then another is produced in a similar manner outside of it. The process is repeated until a sphere, about six inches in diameter, is produced. By and by the film is removed from the wooden former, and is sent into commerce as what is called a bottle.

Vegetable juices containing rubber, or similar hydrocarbons, are cured in other ways in some parts of the world : by drying in the sun ; by boiling in kettles ; by mixing with brine, alum, etc.

The best rubber comes from the district of Para on the lower Amazon, but rubber of similar character is produced from the milky juice of many kinds of trees growing in many parts of the world.*

Rubber is classified in trade as *Paras* (from Brazil), *Centrals* (from Central America), *Africans* (from many points on that continent and its adjacent islands), *East Indians* (from regions in and about India).

Paras are classified as fine new, fine old, medium, coarse new, coarse old, upriver fine, upriver coarse, Caucho, Ceara, Peruvian, Bolivian, Matto-Grosso, Manoa, Mangabeira (Bahia).

Centrals are classified as Esmeralda, Guayaquil, Nicaragua, Cantagena.

East Indians are classified as Borneo, Assam, Penang, Pontianak, Siam, Padang (Sumatra).

Africans are classified as St. Paul de Loando, Gambia, Sierra Leone, Benguela, Kongo, Cameroon, Accra, Liberian, Madagascar pinky or black, Calabar, old Calabar, Batanga, Salt Pond (Cape Coast), Mozambique, Akassa.

According to the *form* of the raw commercial products they are named as strip, scrap, slab, sheet, flake, lump flake, liver, ball, small ball, sausage, thimble, twist, nigger.

Pure caoutchouc is light in color. It is darkened by the crude methods adopted in its first stages of manufacture. It has been proposed to receive in metallic vessels the juice as it flows from the tree ; then, sealing the vessels, to send them to the United States or to Europe for more intelligent treatment of the gum. Ordinary caoutchouc is very adhesive, freshly cut portions joining very rapidly. When heated moderately, it melts into a viscid mass. At high temperatures it undergoes decomposition, evolving gases, which easily take fire and burn with a luminous but smoky flame. Caoutchouc does not readily dissolve, but it softens in certain liquids of which carbon disulphide is one of the best. Coal-tar naphthas of various kinds, and benzene, are among the best solvents. (See isoprene, p. 46.)

Europeans appear to have had their attention attracted to caoutchouc first in 1736 by La Condamine, who was a member of a commission sent by the French government to measure a degree of the meridian in South America. He sent to France some samples of caoutchouc under the name of gum elastic. He noted that the material was employed by the people of Brazil for use not only in torches but also for bottles, overshoes, waterproof fabrics, and even rude syringes. In Europe the caoutchouc soon came into use by artists and others

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* See U. S. Special Consular Report. India Rubber. Washington, D. C., 1892.

for erasing pencil marks.   The English chemist Priestley, in one of his essays, speaks of the substance in connection with the last mentioned use.

In 1797, an English manufacturer named Johnson patented a process for making cloth waterproof by the use of rubber.   He softened the material in a mixture of turpentine and alcohol, and spread the paste so produced upon cloth. He even went farther, in that he spread over the gummy surface the fine textile powder known as "flocks."

In 1819, a Scotch manufacturer, Macintosh by name—who was using large quantities of ammoniacal liquors from gas works and was seeking a commercial outlet for the naphtha of the gas manufacture—conceived the idea of using this naphtha as a solvent for caoutchouc, intending to spread the varnish so produced upon cloth, thereby rendering it waterproof.

In 1825, rude overshoes of caoutchouc were brought to the United States from Brazil, many of them made upon lasts shipped from Boston.   Large quantities of such galoshes* were exported, notwithstanding the fact that they were of a very rude shape and that they became very soft when exposed to heat and very hard when cooled.

The greatest improvement in the treatment of India rubber was that invented by Charles Goodyear and patented by him in 1844; namely, the process called vulcanizing.   Goodyear observed that when caoutchouc is mixed with sulphur and the mass heated, the properties of the substance are materially changed. The small amount of sulphur, say five or ten per cent., enables the rubber article, while still preserving the valuable property of being impervious to water, to retain its pliability when cold.   This is the general principle still underlying the vulcanizing process.   Goodyear also noted that a much larger amount of sulphur, say fifty per cent., produces the article now well known as hard rubber or ebonite.   This substance is now very much employed for an immense variety of articles of daily use.   One of its most valuable properties from the scientific point of view, is the fact that when briskly rubbed with certain dry materials, it becomes highly electrified.

At the present day, vast quantities of caoutchouc products are employed in manufactures.   Hard rubber is employed for a multitude of small articles, like buttons, penholders, combs, handles for various pieces of apparatus.   The characteristic valuable qualities of hard rubber are cleanliness, imperviousness to liquids, elasticity, lightness as compared with metals, and finally a certain ease of manufacture.

The characteristic qualities of ordinary vulcanized rubber are great imperviousness to liquids and gases, high insulating power for electrical appliances.   This variety of rubber has so many and such well known uses that it is unnecessary to specify them.

In general, the process of manufacture of rubber articles, such as boots and shoes, is as follows :

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* The word *galoche* occurs in Piers Plowman.   Chaucer says " unbokel his *galoche*."

First, the gum is *washed* by soaking in hot water and subsequently passing it between rollers under a small stream of water.

Second, it is *sheeted* by passing it through another set of powerful rollers. As a result it forms a coherent but irregular sheet.

Third, it is *dried*, to remove all moisture.

Fourth, it is *compounded*, that is, it is again passed between another set of powerful rollers, in presence of certain substances to be mixed with it. The latter may be looked upon as either mere diluents, or adulterants, or coloring matters, or, it may be, sulphur to accomplish the vulcanizing. Oxide of zinc, a white powder, may be used to produce light colors; sulphide of antimony, to produce red colors; lamp black, to darken; second-hand rubber goods, to cheapen. In this process, the rolls between which the rubber passes revolve at different rates of speed. Thus, the mixture is worked out into thinner and thinner sheets.

Fifth, from the sheets just mentioned, the manufactured article, say a rubber boot, may be formed, the different portions being cemented together.

Sixth, the object is placed in a suitable oven to be vulcanized.

Seventh, before going into the market, the article may be varnished.

Rubber goods for mechanical, medical, and other uses, are made by but slightly different processes.

Gutta percha, although resembling caoutchouc in some respects, such as capacity for resisting liquids, and capability of vulcanizing under the influence of sulphur and heat, is a very different material from India rubber. It is, however, derived from the juice of a tree (*isonandra percha*), and in its manufacture and treatment, much resembles India rubber. Gutta percha comes from the Orient, especially from Singapore and Borneo.

Gutta percha is not produced in such considerable quantities as is India rubber. It is far superior to the latter, however, as an electric insulating material. Naturally, therefore, the modern development of electricity has largely increased the demand for the substance.

Balata is a valuable vegetable product somewhat analogous to gutta percha. It is obtained from South America. It may be rolled into thin, colorless, odorless sheets, and used for waterproofing purposes without vulcanizing.

CHAPTER XXII.

AROMATIC SUBSTITUTION COMPOUNDS.

Halogen Derivatives.

The aromatic hydrocarbons form an immense number of halogen derivatives with fluorine, chlorine, bromine, and iodine. Some have been referred to already.

From benzene, C_6H_5, may be formed C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, $C_6H_2Cl_4$, C_6HCl_5, C_6Cl_6, and some of these form isomers. In similar fashion other hydrocarbons form derivatives more numerous and more complex; for halogen substitution may take place *in the benzene nucleus*, or *in the fatty side-chain*, or *in both at once*, or *in one or more benzene rings* of composite hydrocarbons of higher series.

Aromatic Nitro-Derivatives.

Nitrobenzene, $C_6H_5NO_2$. This substance is easily produced by the action of fuming nitric acid upon benzene. Considerable heat is evolved by the operation, and it is usual in the manufacture to keep the mixture at a low temperature. The mixing is usually carried on in large iron retorts supplied with mechanical stirrers. The nitrobenzene produced is then run into water, whereby any excess of acid is dissolved in the water; the nitrobenzene falls to the bottom of the vessel, from which it may be drawn off. Generally it is subjected to other washings and finally to distillation which affords the substance in a comparatively pure form.

Nitrobenzene is a yellow liquid having a very strong and rather agreeable odor of bitter almonds. It is sometimes called "essence of mirbane," and as such is considerably employed in toilet soaps. The substance, if inhaled in large quantity as vapor, or if taken into the digestive tract, is distinctly poisonous. Enormous quan-

tities of nitrobenzene are now manufactured for the production of aniline.

Dinitro and *tritritro benzenes* are also known.

Nitrotoluene, $C_6H_4(NO_2)CH_3$. This substance, which corresponds in general with nitrobenzene, is prepared by the action of fuming nitric acid upon toluene. The product, which gives off an odor similar to bitter almonds (as does nitrobenzene), may be subjected to subsequent purification. It also produces several toluidines by treatment closely corresponding with those whereby nitrobenzene is reduced to aniline.

Dinitro and *trinitrotoluenes* are also known.

Nitronaphthalene, $C_{10}H_7 \cdot NO_2$. Several nitronaphthalenes are known — mono-, di-, tri-, tetra-, according to the conditions of nitration. They may be produced by a properly regulated direct action of nitric acid.

They are generally prepared *indirectly*, for example, by action of nitric acid on sulphonic or other compounds previously obtained.

Aromatic Amines, etc.

When aromatic nitro compounds are subjected to the action of nascent hydrogen they undergo a change called reduction. This reduction may proceed step by step: oxygen being gradually withdrawn from the molecule, and, at length, hydrogen added. The important series of compounds thus producible may be illustrated by the following list of benzene derivatives due to such reduction :

Nitrobenzene (two molecules),	$C_6H_5 \cdot NO_2$
	$C_6H_5 \cdot NO_2$
Azoxybenzene,	$C_6H_5 \cdot N$
	$C_6H_5 \cdot N$ ⟩O
Azobenzene,	$C_6H_5 \cdot N$
	$C_6H_5 \cdot N$
Hydrazobenzene,	$C_6H_5 \cdot NH$
	$C_6H_5 \cdot NH$
Aniline (two molecules),	$C_6H_5 \cdot NH_2$
	$C_6H_5 \cdot NH_2$

Phenylamine, or *amidobenzene (aniline),* $C_6H_5NH_2$. The name aniline is derived from the Spanish word anil (one form of a similar oriental word) for indigo. This name was assigned because aniline was first obtained (by Unverdorben in 1826) by the dry distillation of indigo. The compound was subsequently discovered in coal-tar. Aniline is one of the most important substances employed in the manufacture of colors. Consequently, it is now manufactured on a large scale. It is produced by some convenient *reducing* process applied to nitrobenzene. Several reduction processes have been employed, for example, such combinations as zinc and hydrochloric acid, iron filings and acetic acid, iron filings and hydrochloric acid, have been used. The effect of all these processes is the liberation of nascent hydrogen, a part of which withdraws oxygen from the nitrobenzene, and a part of which takes the place of this oxygen.

On the large scale, aniline may be produced by use of a large iron tank provided with a stirrer and with suitable openings. The hydrochloric acid, the iron, and the nitrobenzene, are introduced; the stirrer is set in motion, and the mass is gently heated. Reaction sets in promptly, and aniline is produced. At the same time, this substance, which acts like a compound ammonia, combines with some of the hydrochloric acid to produce a chloride, called aniline hydrochloride, C_6H_7NHCl. This latter substance is a solid salt which is considerably used in commerce under the name of aniline salt. The mass in the iron tank is removed and decomposed by lime. The lime withdraws the hydrochloric acid; and the aniline, called aniline oil, is separated from the mixture by distillation.

Aniline as it appears in commerce is called aniline oil, for it is a liquid. It possesses a peculiar and somewhat agreeable odor. At a temperature slightly below zero it solidifies. It becomes brown in color upon exposure to light and air. Its general chemical action corresponds to that of ammonia gas. It may be readily detected in aqueous solution by adding a water solution of sodium hypochlorite (easily prepared from sodium carbonate and bleaching powder). The aniline changes to a blue substance which colors the liquid. If no coloration appears, an addition of a few drops of dilute ammonium sulphide may develop a red color which may be likewise considered the test for aniline.

Aniline is distinctly poisonous, serious effects having followed the inhalation of considerable quantities of its vapor.

Aniline forms a large number of salts with ordinary acids. It

also manifests its relationships to ammonia by producing a corresponding double platinum salt.

Aniline is the starting point for the production of a very large number of derivatives. In many of them, methyl, ethyl, or both, or other radicles in addition, replace the appropriate number of atoms of hydrogen of the aniline.

Amidotoluenes, or *toluidines*, $C_6H_4(CH_3)NH_2$. The formula at once shows that as in the case of other amido compounds, several toluidines are possible. They are produced in general as are anilines; that is, by the reduction of nitrotoluenes.

Naphthylamine, $C_{10}H_7 \cdot NH_2$. Many such amines are known. They are prepared by reduction of nitro- compounds.

Anthramine, $C_6H_4 : (C_2H_2) : C_6H_3 \cdot NH_2$. This is the amido anthracene corresponding to amidobenzene (aniline).

Azo- and diazo- compounds. A great number of substances of these classes are known. Many of them are directly or indirectly of great importance in the production of the artificial organic colors so largely used. Their characteristic feature is the possession of the group — N : N —.

Examples of azo compounds are :

Azobenzene,	$C_6H_5 \cdot N_2 \cdot C_6H_5$
Benzeneazonaphthalene,	$C_6H_5 \cdot N_2 \cdot C_{10}H_7$
Azonaphthalene,	$C_{10}H_7 \cdot N_2 \cdot C_{10}H_7$

The *azo compounds* are produced by a variety of operations, but in general by the action of mild reducing agents on the appropriate nitro aromatic compounds, or by the action of diazo compounds on appropriate amines and phenols. (Generally the diazo compounds are not *separately* formed, but are produced in presence of the amines or phenols — the solutions being kept cool by ice or otherwise during the operation.)

Azo compounds are called primary, secondary, tertiary, according as they contain one, two, or three groups of N_2.

The *diazo compounds* contain the group — N : N — but it is usually attached to only *one* hydrocarbon radicle. They exist only as compounds containing radicles such as hydrogen, chlorine, amidogen, etc. The diazo compounds are usually formed by action of nitrous acid or of some compound that can easily generate it, e. g. sodium nitrite and a mild acid, upon amido compounds.

11

When nitrous acid acts upon ammonia gas, the group N_2 is liberated in accordance with the following equation :

$$NH_3 \ + \ HNO_2 \ = \ N_2 \ + \ 2H_2O$$
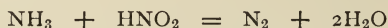
When, however, in place of NH_3, the corresponding organic amido compound (a compound ammonia) is used, instead of the nitrogen being liberated, *it enters as a constituent of the new product.*

Examples of diazo compounds are :

Diazobenzene nitrate,	$C_6H_5 \cdot N_2 \cdot NO_3$
Diazophenol nitrate,	$C_6H_4(OH) \cdot N_2NO_3$
Diazobenzene sulphonic acid,	$C_6H_4 \big\langle {SO_3 \atop N_2} \big\rangle$
Diazonaphthalene sulphonic acid,	$C_{10}H_6 \big\langle {SO_3 \atop N_2} \big\rangle$
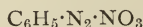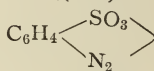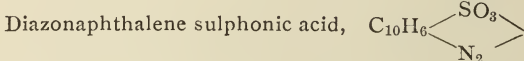
An enormous number of azo coloring compounds are now produced by a diazotising process whereby the operation goes on in presence of two very different aromatic compounds (great range being practicable — various phenols, naphthols, amines, sulphonic acids, acids, etc., being used).

Azines contain N_2, but with the structure $\begin{matrix} -N- \\ | \\ -N- \end{matrix}$

Aromatic Oxygen Compounds.

Quinone, benzoquinone, $C_6H_4O_2$ or
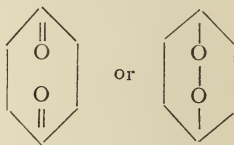
Naphthaquinone, $C_{10}H_6O_2$
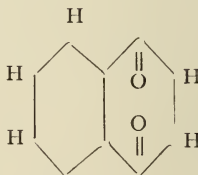
Anthraquinone, $C_{14}H_8O_2$
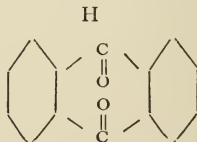
Dioxyanthraquinone (alizarin), $C_{14}H_8O_4$, is an orange colored substance not readily soluble in water or dilute acids. It dissolves, however, in alkaline liquids, producing a magnificent purple color. Alizarin tends to combine with oxides of the metals (with calcium oxide, producing calcium alizarate as a purple precipitate.)

From alizarin, by the use of chemical agents, a large number of derivatives, many of them colored, have been produced.

Alizarin is one of the coloring matters obtained from the madder root. It does not exist ready formed in the root; it exists there as a glucoside called rubian, which produces glucose and alizarin under the influence either of a special ferment (also in the root) or of dilute acids. The madder root has long been used in India and many parts of Europe as a dye stuff.

Two German chemists, Graebe and Liebermann, while experimenting upon alizarin from madder, discovered that it could be decomposed so as to yield a hydrocarbon called anthracene, previously recognized as existing in coal tar. Thereupon they undertook to turn anthracene back into alizarin, and as a result of earnest labor and a certain amount of good fortune they succeeded.

First. The process of Graebe and Liebermann for making alizarin was somewhat as follows:

Starting with anthracene, they oxidized it into anthraquinone. Next they turned anthraquinone into dibromanthraquinone; they heated this substance with potassium hydroxide, thus forming potassium alizarate; they decomposed the potassium alizarate with hydrochloric acid, and thus obtained alizarin. In certain of their operations, where several isomers were possible, they had the good fortune to produce the particular isomer necessary. It has since become apparent that if they had hit any one of several other isomers, the artificial production of alizarin might have been long delayed.

Second. Alizarin is at present produced by a process which dispenses with bromine. It is, in brief, as follows:

Anthracene is oxidized, by use of sodium dichromate and sulphuric acid, into anthraquinone; anthraquinone is sulphonated, by fuming sulphuric acid into anthraquinone sulphonic acid; the sulphonic acid is fused with sodium hydroxide under pressure in a closed vessel, to form sodium alizarate; the sodium alizarate is decomposed by hydrochloric acid to form alizarin.

Phenyl ether, $C_6H_5 \cdot O \cdot C_6H_5$. This substance corresponds in type of structure with the fatty ethers. Although rather a stable compound, one radicle in it may be replaced by an alkyl radicle, thus giving rise to a series of aromatic *mixed ethers*. (Compare with the fatty ethers, p. 76)
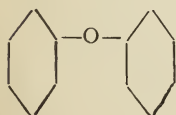
Aromatic Compounds Containing Hydroxyl.

An enormous number of such compounds are known. The names employed are various, but they generally have the syllable *ol* (alcohol designation) at the end of some part of the name. Of course one or more molecules of hydroxyl may be attached to the nucleus; moreover, one or more other radicles may be attached at the same time. Again, when an aromatic hydrocarbon has side chains the hydroxyl may be attached either to the nucleus or to the side chain, thus affording at least two sets of compounds. Hydrosulphuryl, HS, accomplishes a series of similar substitutions.

$C_6H_5 \cdot OH$	Phenol (carbolic acid)
$C_6H_5 \cdot SH$	Phenyl sulphydrate (phenyl mercaptan)
$C_6H_5 \cdot CH_2OH$	Benzyl alcohol (a toluene derivative)
$C_6H_4(CH_3)OH$	Cresol (a toluene derivative)
$C_6H_4(OH)_2$	*(Ortho)* catechol (from catechu)
"	*(Meta)* resorcinol
"	*(Para)* quinol (hydroquinone)
$C_6H_3(OH)_3$	1-2-4 Pyrogallol (pyrogallic acid)
$C_{10}H_7 \cdot OH$	*Alpha and beta*, naphthol
$C_{14}H_9 \cdot OH$	Anthrol

Phenol, also called carbolic acid, $C_6H_5 \cdot OH$. This substance is obtained by processes of distillation and washing, and sometimes by crystallization, from coal-tar. Phenol may be produced, however, by a variety of chemical processes. Some of the phenol furnished in trade is of a very high degree of purity, appearing as white crystals. Other specimens contain certain aromatic compounds which lead it to become red-colored and to deliquesce when exposed to the air. The pure article, however, does not redden under the influence of light and air.

Phenol, or carbolic acid, is largely employed as a disinfectant or germicide. Sometimes it is used mixed with water or other materials; as for instance, diffused through soap. In some sur-

gical operations, a spray of the aqueous solution is employed, with excellent effect, with a view to the prevention of the growth of microbes. It is not now considered, however, as efficient an anti-septic as it was formerly thought to be. It is a very violent poison, when taken into the system of the higher animals, and cases of poisoning often occur when it is accidentally or intentionally administered. It is considerably used in the manu-facture of salicylic acid, also of picric acid, aurin, azo-colors, etc.

Phenol was formerly regarded as an acid (carbolic acid) because it forms combinations with sodium, potassium, and other metals. These compounds are still called carbolates or phenates. It has also been viewed as an alcohol, because it contains the hydroxyl group OH. It is now, however, placed in a new class—the phenols—of which itself is the typical compound.
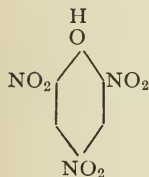
Picric acid, trinitrophenol, $C_6H_2(NO_2)_3OH$. Picric acid is not usually manufactured by the direct action of any acid on phenol. Instead, a sort of intermediate product, phenol-sul-phonic acid is employed. On the large scale, phenol is mixed with sulphuric acid and nitric acid. In due time, crystals of picric acid separate from the mixture as brilliant yellow scales. They are subjected to subsequent purification.

Picric acid is largely used in the arts. Its most marked characteristic, after its intensely bitter taste, is its power of dyeing animal matters yellow. It colors the skin, fibres of silk or of wool, portions of quill, portions of leather. It does not, however, readily color *cotton* and other vegetable fibres. Picric acid is exceedingly poisonous. Notwithstanding this fact it is said that minute quan-tities of it are sometimes used in beer to impart bitterness.

Picric acid is used to some extent to produce picrates for employment in cer-tain kinds of gunpowder and similar explosives.

Pyrogallol, $C_6H_3(OH)_3$, (1-2-4). This substance, commonly called pyrogallic acid, is produced as a sublimate when gallic acid, $C_6H_2(OH)_3COOH$, is heated. Pyrogallol has to a marked degree the power of absorbing oxygen. A solution of the substance in potassium hydroxide is very efficient in this way. Indeed it is often used in gas analysis for absorbing oxygen from its mixture with other gases.

This affinity of pyrogallol for oxygen leads it also to reduce compounds of the metals, of gold, silver, and mercury, for example.

On this account pyrogallol is considerably used in photography as a developer.

The oxidation of pyrogallol and its compounds generally affords dark-colored products.

Cresol $C_6H_4(CH_3)\cdot OH$, is a hydroxyl substitution product of toluene, $C_6H_5\cdot CH_3$, just as phenol is a similar product of benzene, C_6H_6. Many cresols are known.

It has long been noticed that when certain substances, such as coal and wood, are distilled for the production of gas, certain of the oils condensed are capable of coagulating albumen and that they prevent putrefaction. On account, then, of the power of preserving meat, the name creasote has been applied to them. The word is derived from two Greek words (κρέας, kreas, meat ; and σώζω, sozo, to preserve). Chemists have carefully studied the creasote derived from the distillation of wood and that derived from the distillation of coal, and have discovered that while they have a general resemblance, both consisting of mixtures of water with various aromatic compounds, yet they have important differences. It is now known that the creasote of wood contains cresol, or cresyl alcohol, which is different from phenol, but has a general correspondence with it.

Naphthol, $C_{10}H_7\cdot OH$. Members of the α- and β series are known. They are prepared in general by fusing the proper sulphonic acids or the proper sulphonates with caustic soda or potash.

The napthols are the starting points of an immense series of products which, while retaining the hydroxyl group, may be sulphonated, nitrated, reduced to amides, azotized, diazotized, etc.

Anthrol, $C_6H_4(C_2H_2)C_6H_3\cdot OH$. This substance is prepared by fusing anthracene sulphonic acid with potassium hydroxide.

Aromatic Acids : Carboxylic and Sulphonic Acids.

Carboxylic acids. The aromatic hydrocarbons form the bases of an enormous number of acids. In some of them, one or more groups of carboxyl, COOH, exist. This radicle may, however, be attached either to the ring nucleus or to the side-chain ; thus its position involves two sets of carboxylic acids. Of course such acids form salts with metals.

Carboxylic Acids. First Series.

mono		benzoic acid,	$C_6H_5 \cdot COOH$
di	1–2	phthalic acid,	$C_6H_4 (COOH)_2$
	1–3	isophthalic acid,	"
	1–4	terephthalic acid,	"
hexa		mellitic acid,	$C_6 (COOH)_6$

Carboxylic Acids. Second Series.

Phenylformic acid,	$C_6H_5 \cdot COOH$	(benzoic acid)
Phenylacetic acid,	$C_6H_5 \cdot CH_2 \cdot COOH$	
Phenylpropionic acid,	$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH$	(hydrocinnamic acid)
Phenylacrylic acid,	$C_6H_5 \cdot CH : CH \cdot COOH$	(cinnamic acid)

Benzoic acid, C_6H_5COOH. This substance is formed by the dry distillation of gum benzoin. This gum is obtained as the result of incisions in the trunk of a tree growing in oriental countries. The benzoic acid may be separated from the gum by distilling the latter in a suitable vessel. The benzoic acid sublimes in the form of delicate white crystalline flakes. Benzoic acid is now manufactured from aromatic compounds and may be produced synthetically. Benzoic acid forms a large series of salts as well as many derivatives.

Mellitic acid, $C_6(COOH)_6$. This is prepared from honeystone, a mineral (containing an aluminium salt of mellitic acid) occurring in certain seams of brown coal.

Salicylic acid, $C_6H_4(OH)COOH$. This acid occurs in certain plants (*spiræa*). The compound methyl salicylate occurs in oil of wintergreen (derived from *gaultheria*). The acid is now made in large quantity, by Kolbe's process, from phenol, C_6H_5OH. The phenol mixed with caustic soda is subjected, under special conditions, to carbon dioxide gas, CO_2. The first product, which is impure, is purified by crystallization, etc.

The substance forms white crystals. It produces a series of salts. It is used as an antiseptic. (Its power appears to be due to the fact that it readily decomposes into phenol and carbon dioxide.)

Gallic acid, $C_6H_2(OH)_3COOH$. This acid exists in nutgalls and certain other astringent vegetable matters (usually mixed with a variety of other substances). The acid may be extracted from nutgalls or it may be prepared artificially.

Gallic acid is a white crystalline substance. It forms a series

of gallates. With ferric salts it produces black precipitates (writing inks) which, however, easily dissolve.

Gallic acid by heating produces pyrogallol and carbon dioxide.

Gallic acid does not precipitate gelatine solutions as tannic acid does.

Tannic acid or *tannin*, $C_6H_2(OH)_3COO \cdot C_6H_2(OH)_2 \cdot COOH$. The term tannin has been applied in general to the astringent substance which exists in a large number of vegetable products suitable for tanning animal skins to produce leather. Such products are nutgalls, leaves and twigs of sumach, oak bark and other barks, catechu, gambier, etc.

In solutions of gelatine, tannic acid produces an insoluble precipitate, and it is assumed that such a precipitate, more or less completely formed in the animal hide, performs an important part of the operation of producing leather.

Of late an entirely new method of tanning has been successfully introduced. By it, the skins are soaked first in a solution of potassium dichromate and hydrochloric acid. After the chromic acid has saturated the skins, they are drained, and then introduced into another bath containing sodium hyposulphate. As a result, a green chromium oxide is produced, which combines with the hide fibre to produce a very stable compound.

Ink. Tannic and gallic acids are very much used in the preparation of inks. Indeed, it is now believed that for permanency no inks surpass those containing gallic principles and iron. The advantage consists in the fact that the iron compounds remain for a long time in the paper; and even if the coloring matter is faded, the application of some substance, like potassium ferrocyanide, will make the faded writing legible; the reason is found, of course, in the fact that the iron then produces Prussian blue.

In the manufacture of ordinary black ink, crushed nut galls, ferrous sulphate, gum arabic, and water, are employed. The galls and the iron produce a very finely divided precipitate having a black or blue-black color. The gum arabic thickens the liquid slightly, and so prevents the subsidence of the precipitate. In order to avoid mould, a great many substances have been recommended as additions. Oil of cloves, salicylic acid, mercuric chloride, are examples. Instead of nut galls, certain cheaper dyeing materials, such as logwood extracts, are often employed in inferior inks. Sometimes indigo solutions, or other soluble coloring matters, are employed. Thus, in many cases at the present day, coal tar coloring matters are used. Printers' ink derives its color from lamp black. India ink is made from the same material.

Indelible ink is usually an ammoniacal solution of silver salts, colored

slightly with indigo. The silver compound is decomposed by the organic matter of the cloth; and there is produced either metallic silver, black by reason of its fine state of division, or else some black compounds of silver.

The Sulphonic Acids.

Sulphuric acid applied directly or indirectly, under varying conditions, forms sulphonic acids, with not only hydrocarbons, *but also with a multitude of their substituted derivatives.* In all these acids the characteristic feature is the sulphonic group, SO_3H, of which one or more molecules may be present in a given case. The hydrogen of this group is replaceable by a metallic element, thus forming salts—the sulphonates. These sulphonic acids and sulphonates are largely used as intermediate compounds in progressing from a certain compound in hand, to one whose formation is desired.

Benzene sulphonic acid, $C_6H_5 \cdot SO_3H$. This substance is produced in a variety of ways, the simplest being by the direct action of sulphuric acid on benzene. The compound is a deliquescent solid. It forms a variety of compounds — with metals and with other hydrocarbon radicles.

Three disulphonic acids are known, o, m, and p. These also produce an immense number of derivatives.

The other hydrocarbons of the benzene series also produce sulphonic acids and derivatives.

Naphthalene sulphonic acid, $C_{10}H_7 \cdot SO_3H$. This substance is prepared by direct action of sulphuric acid on naphthalene; a- and β- forms are known. Many other sulphonic acids of naphthalene are known.

Anthracene sulphonic acid, $C_{14}H_9 \cdot SO_3H$. Many such sulphonic acids are known.

The sulphonic acids already mentioned represent some of the simplest products of the style of combination under discussion. Other acids formed from aromatic nitro, amido, hydroxyl, and other substitution compounds — or from compounds in which several different radicles enter at once — are known, and they are of great importance in the artificial organic color industry.

Saccharine, anhydro-sulphamido-benzoic acid, $C_6H_4 \underset{SO_2}{\overset{CO}{<}} {>} NH.$
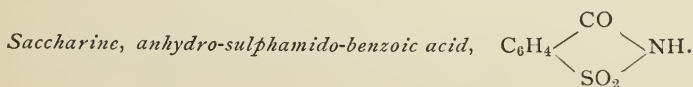
This substance is a solid, soluble in water, and about five hundred times as sweet as cane sugar. In general it is produced as follows: toluene is changed into toluene sulphonic acid; then this is oxidized into sulphobenzoic acid; then this is chlorinated into sulphobenzoic acid dichloride; then this by action of ammonium carbonate is changed into sulphamidobenzoic acid; then this by mild acid treatment forms the saccharine. (The latter trivial name is an unfortunate one, but it is in use.)

Saccharine is used somewhat in medicine, and for the sweetening of foods for patients who are not allowed to take cane sugar. It is not itself in any sense a food, for it has been found to pass through the animal organism unchanged.

Artificial Organic Coloring Matters.

This title is intended to be more comprehensive than the term aniline colors (chiefly aniline derivatives); more even than coal-tar colors. This latter term is a convenient and appropriate one, for the chief raw materials for the artificial organic colors come from coal-tar.

In 1826 Unverdorben produced aniline by the destructive distillation of indigo. Soon after, the substance was detected in coal-tar, ready formed. It is now made in enormous quantities indirectly (that is from benzene) from coal-tar. In 1835 Runge observed that a beautiful violet-blue color is produced when bleaching powder acts on aniline. In 1856, W. H. Perkin isolated a magnificent color, which he called *mauve*, which he had produced by this general class of reactions. Later A. W. Hofmann and many others studied the constitution of this class of colors, the conditions under which they are formed, and the various methods of production; these researches led to the development of the aniline color manufacture, and they laid the foundations for the important organic color industries of the present day. In 1868, Graebe and Liebermann produced artificial alizarine from anthracene of coal-tar, (and later W. H. Perkin made valuable improvements in the process employed.) This most important synthesis has been followed by the production of a magnificent series of alizarine derivatives. These noteworthy achievements have been followed by the production, in rapid succession, of new aromatic colors, bewildering in number and complexity. To-day there are several very large color factories (employing large corps of chemists, of the highest degree of skill), and manufacturing daily new and, if possible, yet more useful products. It is worthy of remark that the industrial production of colors on a large scale has advanced

the *theoretical* chemistry of this department, far more than mere laboratory experiments could possibly have done.

The following important general principles as to organic coloring compounds have been formulated :

1. Practically all the natural as well as artificial organic colored bodies are benzene derivatives.

2. The aromatic hydrocarbons are colorless.

3. Hydrocarbon derivatives in which *one atom* of hydrogen is replaced by hydroxyl, HO, the nitro group, NO_2, the amido group NH_2, are colorless. The same is true when two replacing groups just alike are present.

Thus phenol, C_6H_5OH, nitrobenzene, $C_6H_5NO_2$, aniline, $C_6H_5 \cdot NH_2$, are colorless.

4. Mixed di-derivations of the classes mentioned are sometimes colored, sometimes not.

Thus trinitrophenol (picric acid) $C_6H_2(OH)(NO_2)_3$, is yellow; nitraniline, $C_6H_4(NH_2)NO_2$, is yellow.

5. Color appears to be dependent upon certain molecular groups and arrangements. Groups of this character are called *chromophors*. Among the most important chromophors are :

—O—O— in quinones,

—N : N— in azo compounds.

—NO_2 in nitro compounds,
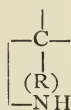
$$\begin{matrix} | \\ -C- \\ | \\ (R) \\ -NH \end{matrix}$$ A methane substitution group existing in mauve, fuchsine, (magenta, solferino,) and similar compounds of the triphenylmethane series.
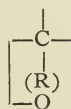
$$\begin{matrix} | \\ -C- \\ | \\ (R) \\ -O \end{matrix}$$ Existing in the aurins.
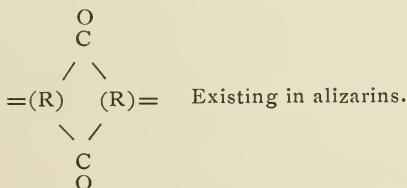
$$\begin{matrix} O \\ C \\ / \quad \backslash \\ =(R) \quad (R)= \\ \backslash \quad / \\ C \\ O \end{matrix}$$ Existing in alizarins.

6. In all these cases, the chromophors, when linking aromatic groups of the most varied kinds produce *chromogenes*. These chromogenes are not *dyes :* they become dyes on the substitution, in the aromatic radicles, of certain special groups like OH and NH_2.

Thus —N : N—   is a chromophor
    Azo benzene   (yellow) $C_6H_5 \cdot N_2 \cdot C_6H_5$ " chromogene
    Amidoazobenzene (yellow) $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH_2$ " dye

(The hydrochloride of amidoazobenzene was formerly sold under the names aniline yellow, spirit yellow. It is not now used except as a starting point for more complex and more serviceable colors)

7. Generally the salts of dyes have stronger colors than the dyes themselves: thus the acid dyes give stronger colors when united with metallic radicles—and the basic dyes when united with acid radicles:

Sodium picrate is more intensely yellow than picric acid; the salts of the base, rosaniline, are more deeply colored than the hydrate of that base.

8. Increase of number of salt forming groups, increases depth of color:

Amidoazobenzene	$C_{12}H_9N_2(NH_2)$	is yellow
Diamidoazobenzene	$C_{12}H_8N_2(NH_2)_2$	is orange
Triamidoazobenzene	$C_{12}H_7N_2(NH_2)_3$	is brown

9. When the hydrogen of amidogen, NH_2, is replaced by hydrocarbon radicles the color often advances in shade in a particular direction: thus corresponding salts

of Rosaniline	$C_{20}H_{19}N_3$	are red
of Phenylrosaniline	$C_{20}H_{18}(C_6H_5)N_3$	are red-violet
of Diphenylrosaniline	$C_{20}H_{17}(C_6H_5)_2N_3$	are blue-violet
of Triphenylrosaniline	$C_{20}H_{16}(C_6H_5)_3N_3$	are blue

A recent list by Schultz and Julius names and describes 392 such colors, now or recently manufactured. (This number includes, of course, colors capable of practical use in the arts; probably many thousands of colored compounds of the aromatic series may be made by methods now understood, but certain principles are now recognized which indicate beforehand that most of them are commercially useless.)*

The coal-tar colors are classified by the dyer and colorist according to *technical* standards, that is, according to their solubility or insolubility in water or alcohol, according to their applicability to cotton or to wool or to silk, and otherwise. The chemist prefers to classify them according to their plan of structure and according to their *chemical* relationships.

Schultz and Julius arrange artificial organic dyes in groups as follows:

1.	Nitro-compounds,	15	mentioned.
2.	Azoxy "	3	"
3.	Hydrazone-compounds,	1	"
4.	Azo "	212	"
5.	Nitroso "	5	"
6.	Oxyketone "	23	"

---

* Schultz, G. and Julius, P.; Tabellarische Uebersicht der Künstlichen organischen Farbstoffe Berlin, 1891. It contains dates of the discovery of individual colors, patents, etc.

7.	Diphenylmethane compounds,		3	mentioned.
8.	Triphenylmethane	"	75	"
9.	Indophenol	"	2	"
10.	Oxazine and Thiazine	"	12	"
11.	Azine	"	18	"
12.	Artificial indigo	"	3	"
13.	Quinoline	"	7	"
14.	Acridine	"	4	"
15.	Thiobenzyl	"	3	"
16.	Of unknown constitution,		6	"

$$392$$

The nitro compounds. These tend to produce yellow and orange dyes.

Picric acid, which is trinitrophenol, is a good illustration. *Brilliant yellow* is a sodium salt of dinitro *a*- naphthol-monosulphonic acid,
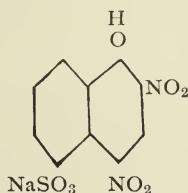
The azo compounds. The number of these mentioned shows their relative importance. They produce nearly all colors — many yellows, oranges, and browns, reds, greens, blues, and even blue-blacks. The most varied aromatic hydroxyl, and amido, and sulphonic compounds, especially of the naphthalene series, are diazotized and combined to produce the azo dyes. (See p. 161.)

Rosazurin (Bayer) which dyes cotton a bluish-red is an azo-compound, viz. :

Sodium sulphonate of methyl-β-naphthylamine-azo-ortho-toluene-toluene-azo-methyl-β-naphthylamine sodium sulphonate :
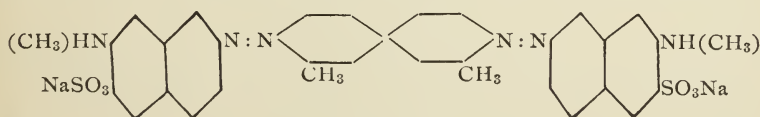
The oxyketone compounds. These include chiefly, the alizarin compounds and other anthracene derivatives. (See p. 163.)

The triphenylmethane compounds. As the name suggests, the

structure of the fundamental molecule of such compounds is methane (marsh gas) CH_4, in which three atoms of hydrogen are replaced by three molecules of phenyl, C_6H_5.

$$C_6H_5$$
$$|$$
$$H-C-C_6H_5$$
$$|$$
$$C_6H_5$$
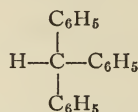
Triphenylmethane

But in the coloring compounds of this group there is *first*, an amidogen replacement on the phenyl ring, *second*, a hydrocarbon replacement in one or more of these amidogens (see p. 172), *third*, a special linkage in the chromophor (see p. 171), *fourth*, an acid radicle combining with the whole base formed by the substitutions first described.

Thus parafuchsine is $C_{16}H_{18}N_3Cl$.

Ordinary fuchsine (called magenta, solferino, and by other names,) has the formula, $C_{20}H_{19}N_3 \cdot HCl$, as shown in the diagram below:
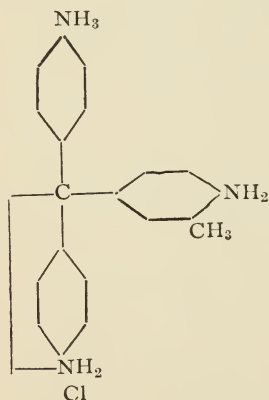
Parafuchsine

Ordinary fuchsine
(Rosaniline hy-
drochloride)
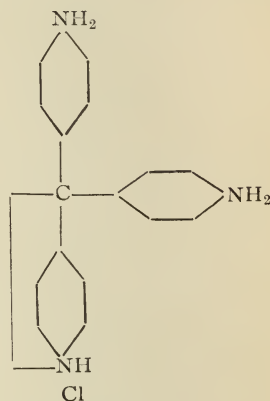
In ordinary fuchsine the presence of CH_3 on one of the rings shows that the compound is a toluidine derivative as well as an aniline derivative. Thus it cannot be made from benzene alone: toluene is necessary in addition.

NH$_2$

|
C —— NH$_2$

CH$_3$

—— NH$_2$OH
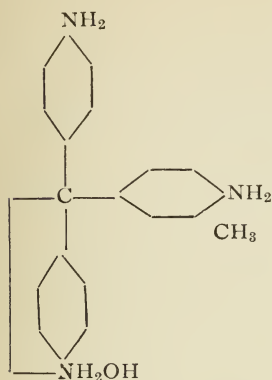
True base of
fuchsine

The *true base* of fuchsine is supposed to have the formula $C_{20}H_{20}N_3 \cdot OH$, with the structure shown in the margin: it is supposed that this base changes, immediately after formation, to the *rosaniline base*, having the same literal formula, but having the hydroxyl in a slightly different position.

The term rosaniline is often used somewhat ambiguously. The relations of a few of the different important compounds which this name involves may be stated as follows in comparison with ammonia compounds:

Parent substance:	ammonia gas,	NH$_3$;	rosaniline,	$C_{20}H_{19}N_3$
True base:	ammonium hy-		rosaniline	
	droxide,	NH$_4$OH;	base,	$C_{20}H_{20}N_3OH$
Chlorine salt:	ammonium		rosaniline chlo-	
	chloride,	NH$_4$Cl;	ride (fuchsine),	$C_{20}H_{20}N_3Cl$

The tetraphenylmethane compounds are produced from a variety of substances, but largely from substitution products of the benzene series.

The colors produced are reds, blues, and violets, of magnificent shades — but yellows and greens are also produced.

C$_6$H$_4$OH

Phenolphthalein, —C—C$_6$H$_4$OH   belongs to this group.

C$_6$H$_4$CO
O
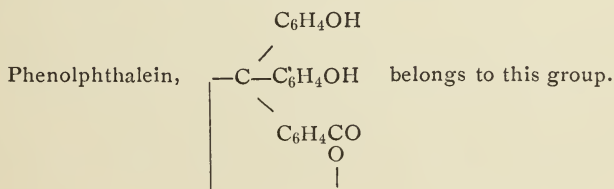
Its weak alcoholic solution is colorless; upon addition of a minute quantity of an alkali a beautiful red color is developed. The substance is useless as a dye; it is only used as an *indicator* in the laboratory.

Substances of unknown constitution. Among these is the im-

portant *aniline black*.   It is supposed to differ in composition
according to the details of the process of its production.   It is
thought to be some kind of salt (often a chromium compound) of
the compound nigraniline, whose formula is taken temporarily as
$(C_6H_5N)_x$.

It affords the fastest and deepest black shades now known.
Its production depends upon the following general principle ;
namely, when aniline salt is mixed with a chlorate, say potassium
chlorate, in presence of some salt of a heavy metal, commonly of
copper or of chromium but better of vanadium, a dark green color
is produced, which becomes black under the influence of a mild
alkali.

This color is largely used upon cotton in calico printing.   In practice, a paste
is made containing aniline chloride, sodium chlorate, a very minute amount of
ammonium vanadate, and starch.   This is printed upon cloth according to the
pattern desired.   The cloth is then dried and allowed to stand for some time,
when it is subjected to ammonia gas, to soap, or some other mildly alkaline
substance.   The color then develops as a deep and permanent black, one that is
not easily injured by the sunlight, by air or moisture, or even by chemical
agents.

CHAPTER XXIII.

CERTAIN NATURAL ORGANIC COLORING MATTERS, etc.

Indigotin, $C_{16}H_{10}N_2O_2$. This is the most important one of the many coloring matters existing in indigo. Indigo is largely produced from the leaves or stems, or both, of a small shrub, *indigofera tinctoria*; but several other plants yield it. Indigo comes chiefly from India, but it is also produced in China, Egypt and Central America. In India the plant is packed in large vats and soaked in water; fermentation sets in; the liquid is drawn off into other vats in which it is violently agitated with paddles, by which the oxygen of the air is introduced; finally the liquid is allowed to rest, whereupon the blue coloring matter subsides. The pasty matter is filtered, and the solid part is pressed into small cubes.

Indigo of commerce contains a variety of compounds : *Indigo-gluten, indigo-brown, indigo-red*, and a glucoside *indican*. When indican is treated with certain acids it yields *indirubin* and *indigotin*, $C_{16}H_{10}N_2O_2$, the latter the most important coloring matter of indigo.

Indigotin may be sublimed as a purple vapor, by gently heating indigo. It may be prepared from indigo-white also.

Indigo-white, $C_{16}H_{12}N_2O_2$, is produced when indigo is subjected to mild reducing agents, in presence of free alkali.

Fritsche's method illustrates its production ; place in a flask :

> 5 gms. finely powdered indigo,
> 10 gms, grape sugar,
> 50 c.c. of a 40% solution of sodium hydroxide,
> 150 c.c. water,
> 300 c.c. 90% alcohol ;

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heat the mixture in a water bath for 30 minutes ; allow the whole to subside. The clear liquid should now contain white indigo. Draw off the clear liquid by means of a siphon into a beaker. Pass into it first a strong current of carbon dioxide, then a current of air; indigotin should now be precipitated.

Under the influence of concentrated sulphuric acid indigotin forms two sulphonic acids—mono- and di-.

Indigotin monosulphonic acid, $C_{10}H_9(HSO_3)N_2O_2$, is insoluble in dilute acids, but soluble in water. Its sodium salt is called *indigo-purple*.

Indigotin disulphonic acid, $C_{10}H_8(HSO_3)_2N_2O_2$, was formerly called sulphindigotic acid. It quickly forms under action of sulphuric acid. When its dilute solution in water is precipitated by common salt a paste called *indigo-extract* is formed. The sodium salt is called indigo-carmine.

Indigotin is converted by oxidizing agents into *isatin*, C_8H_5NO.

Indigotin has been produced by an artificial synthesis (Baeyer).

Alizarin, $C_{14}H_8O_4$. This substance has already been referred to as the chief coloring matter obtained from *madder*, the ground root of *rubia tinctorum*. Madder has long been grown in Asia Minor, and later in various parts of Europe—Italy, France, Holland, Russia. For ages it has been the chief dyestuff used in the manufacture of calico and turkey red in the Orient, and up to the time of the production of artificial alizarin, for the same purpose in Europe and the United States. It has been most carefully studied, and it has been found to contain a great many coloring matters. The chief ones are alizarin, $C_{14}H_8O_4$, and purpurin, $C_{14}H_8O_5$. On calicoes, with different mordants, madder is able to produce blacks, various shades of violet, chocolate, red and pink ; and the colors are very fast.

Moritannic acid, $C_{15}H_{12}O_7$(?). This is one of the coloring matters obtained from the substance known as *fustic* or *old fustic*, the wood of *morus tinctoria*. But the wood contains other coloring substances in addition.

Fustic is essentially a yellow wood. It is used, with mordants containing tin or aluminium, to produce yellow colors. When mixed with other woods, and with mordants containing iron or chromium, it is used to produce shades of brown, olive, etc.

Hæmatoxylin, $C_{16}H_{14}O_6$, etc. This substance is the principal coloring matter obtained from logwood, the wood of *hæmatoxylon campechianum.*

This important dyewood comes from the West Indies. It appears to contain glucosides, which decompose, under proper treatment, into glucose and the true dyeing compounds hæmatoxylin, $C_{16}H_{14}O_6$, (a white substance, which forms colored compounds by combining with metallic oxides) and hæmatein, $C_{16}H_{12}O_6$ (a reddish brown substance produced by oxidation of hæmatoxylin).

Logwood is very largely used for blacks and greys on all sorts of fabrics, principally by use of mordants containing iron or chromium or aluminium.

Brazilin, $C_{22}H_{18}O_7$. This substance is obtained from Brazilwood, a member of the *cæsalpina* family and one of a group of woods—peach wood, lima wood, sapan wood, Pernambuco wood— which are closely allied. They appear to contain glucosides, which yield brazilin. Brazilin oxidizes in the air, producing brazilein, $C_{22}H_{16}O_7$. The woods referred to were much used formerly to produce shades of red and pink.

Santalin, $C_{15}H_{14}O_5$. This substance appears to be obtainable from several varieties of *hard red woods*—red sanders, barwood and camwood. They were much used formerly for producing reds and composite colors, such as brown, etc.

Quercitrin, $C_{21}H_{22}O_{12}$. This is the principal coloring substance derived from *quercitron bark*, the bark of a species of *quercus*. The coloring principles are quercitrin, $C_{21}H_{22}O_{12}$, and quercetin, $C_{24}H_{16}O_{10}$, both yellow substances, which dissolve in alkalies. From quercitron, a yellow, powdered extract called *flavine* is produced. It is used for producing yellows.

Carminic acid, $C_{17}H_{18}O_{10}$. This is the principal coloring compound in the commercial substance known as cochineal, a material consisting of the dried and shrivelled bodies of the female of an insect *coccus cacti*, which lives on a variety of cactus. The plant and insect (natives of Mexico and Guatemala) have been introduced into the Canary Islands, Algeria, Java and Australia. About 70,000 individual insects are required to make one pound of cochineal.

Carminic acid is a purple solid soluble in water, alcohol, and

other solvents. It dissolves in caustic alkalies, producing a splendid purple color. It adheres to certain mineral substances, like aluminic hydroxide, $Al_2O_6H_6$, when they are precipitating, forming *lakes.*

It is largely used for dyeing fast scarlets and crimsons on woolen goods, tin mordants being used.

Alkaloids.

1. The name alkaloid is applied to members of a certain class of substances (about 175 are known) whose representatives are found in plants or natural plant products.

2. In some cases a given plant contains more than one alkaloid. Thus in Peruvian bark 23 different, but closely related, alkaloids have been detected. In opium, from the poppy, as many as 17 have been reported.

3. The alkaloids contain nitrogen in addition to carbon, hydrogen, and oxygen (although three are known which do not contain oxygen).

4. They are all compounds of an aromatic type, that is, their molecules have a ring structure. But they appear to have close relations to the substance called pyridine, and they are often spoken of as pyridine compounds.
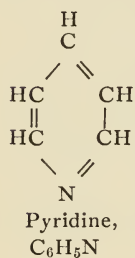
Pyridine, C_6H_5N, is a poisonous, colorless liquid found in coal-tar, in the oil distilled from bones (bone-oil, Dippel's animal oil,) and elsewhere. Its molecule has the structure represented by the adjacent diagram: a benzene ring in which one atom of carbon has been replaced by an atom of nitrogen. Pyridine bears a certain resemblance to ammonia gas: it fumes with hydrochloric acid, uniting with it to form a chloride (or hydrochloride): it precipitates many metals, as hydroxides, from their solutions: it makes a deep-blue solution with copper salts, etc.

Pyridine, C_6H_5N

5. The alkaloids act like ammonia gas in certain ways: they unite directly with hydrochloric acid (and other acids) without evolution of hydrogen, forming a salt or salts

6. The alkaloids and their salts when administered to living animals produce powerful effects: stimulating, or narcotic, or poisonous, or remedial, according to the conditions of their administration. (Hence the portions of the plants, containing alkaloids, manifest these properties, in a modified degree, it may be.)

The following is a list of a few of the more important alkaloids :

I. Alkaloids Without Oxygen.

Coniine, $C_8H_{17}N$.   It exists in poisonous hemlock, *conium maculatum*.

Nicotine, $C_{10}H_{14}N_2$.   It occurs in the leaves of tobacco, and elsewhere.   It is ordinarily a liquid, very volatile, highly poisonous.   Tobacco appears to contain nicotine in very varying quantities.   The amount varies from 1.5 % to nearly 8 %.

Sparteine, $C_{15}H_{26}N_2$.   It occurs in the common broom, *spartium scoparium*.

Curarine, $C_{18}H_{35}N$ (?).   It occurs in a resinous poison used on arrow heads by South American aborigines.

II. Alkaloids Containing Oxygen.

Caffeine or theine, $C_8H_{10}N_4O_2$.   It occurs in certain vegetables, as follows :

Coffee, ...	1. to 1.3 %
Tea, ...	2. to 4. %
Guarana, about	5. %
Maté, about	1.5 %
Kola seeds (when dried), about .	2. %
Cocoa, a small amount.	

Several methods of extraction have been devised.   In general a strong water extract is first made ; then slaked lime is added to free the alkaloid ; next, the alkaloid is dissolved in chloroform or some similar solvent ; upon evaporating the solvent the alkaloid is obtained.

Sweepings from the tea-warehouses of London constitute the raw material.

Theobromine, $C_7H_8N_4O_2$.   It exists in small quantity in the seeds from which chocolate is prepared.

The word *cocoa* is somewhat ambiguous.

The chocolate tree (Theobroma Cacao) produces those seeds which, ground and otherwise prepared, afford the preparations known as chocolate and cocoa. They also afford an oil called cacao butter (cacao pronounced kă-kā′ō).

The cocoanut palm (Cocos Nucifera) produces the fruit called cocoanut.   The wood of the tree, the fibre, the juice and flesh of the cocoanut and its shell, are most useful products.

The coca shrub (Erythroxylon Coca) produces a leaf which, when dried, is an important drug. The shrub grows in South America, and is largely used by the inhabitants as a stimulant. The leaf contains an alkaloid called cocaine, (pronounced kō'kă-in) now largely used in some branches of surgery.

Quinine, etc., $C_{20}H_{24}N_2O_2$. The bark of the cinchonas, especially that of the roots, contains many alkaloids. Some are crystallizable and some are not. The principal crystallizable ones in the bark are quinine and quinidine, cinchonine and cinchonidine. The bark yields approximately as follows, the amounts varying with the kinds of bark :

Of quinine,	.4 to 11.6 % }	$C_{20}H_{24}N_2O_2$.
Of quinidine,	.8 to .9 % }	
Of cinchonine,	.4 to 2.2 % }	$C_{19}H_{22}N_2O$.
Of cinchonidine,	.4 to 5.2 % }	

The trees producing quinine vary in size. Sometimes they are only shrubs of 8 or 10 feet ; in other cases tall trees.

The alkaloid, quinine, is of great value in medicine, having remarkable specific power in the cure of intermittent fevers. The use of the *bark itself* in medicine is now very much diminished. The alkaloids are extracted in a state of greater or less purity, the one chiefly used being quinine, and this in the form of a white salt, a sulphate, often called sulphate of quinia.

Artificial preparation of quinine suggested. It has long been known that quinine under some chemical conditions is decomposed into several substances, one of which is quinoline (C_9H_7N). Now quinoline is found in certain coal-tar products. It has also been produced by Skraup from a mixture of aniline, nitro-benzene and glycerin. The suggestion has naturally arisen that if quinine can be broken down into quinoline, perhaps quinoline can be artificially built up into quinine. This idea receives encouragement from the fact that alizarin has been produced artificially from anthracene. Moreover the great importance and value of quinine and the expense of obtaining it from bark, offer a strong stimulus to investigation looking toward its artificial preparation.

Preparation of quinine.—There are many ways of extracting quinine from the bark. They all involve three general principles : First, quinine combines with hydrochloric, sulphuric or other acids, to form salts ; second, when such salt is treated with lime or other suitable alkali, the acid is withdrawn and the quinine is liberated in a form insoluble in water ; third, the liberated quinine is removed by solution in some suitable solvent, such as ether, alcohol, chloroform, or other liquid of similar general character.

Morphine,	$C_{17}H_{19}NO_3$ }	These, and many others,
Codeine (methyl morphine),	$C_{18}H_{21}NO_3$ }	are derived from opium.
Narcotine,	$C_{22}H_{23}NO_7$ }	

Opium as it appears in commerce is a hardened mass of juice from unripe capsules of the poppy. The supply of the world is derived from Asia Minor, Persia, India, China and Egypt. China is said to consume the larger proportion of the total amount of the opium produced.

Various kinds of opium vary very much in quality. An average statement of the alkaloids is as follows :

Morphine, ...	6. to 15. %
Narcotine, ...	4. to 8. %
Other alkaloids, ...	5. to 2. %

Opium and its preparations are among the most important remedial agents known. Their most valuable constituent is morphine, a white crystallizable substance having a bitter taste. Like other alkaloids it is capable of combination with acids to form salts.

In general, to prepare morphine, the opium is treated as follows : It is macerated with water ; the water extract is filtered and then evaporated ; from the evaporated residue the pure alkaloid is extracted by use of a mixture of alcohol and ether ; this last solution is evaporated, to yield crystals of morphine.

Atropine, $C_{17}H_{22}NO_3$. It occurs in *atropa belladonna,* and in *datura stramonium.* Applied to the eye, it enlarges the pupil.

Cocaine, $C_{17}H_{21}NO_4$. It occurs in the leaves of *erythroxylon coca.*

Strychnine, $C_{21}H_{22}N_2O_2$ ⎫ These alkaloids occur in nux vomica,
Brucine, $C_{23}H_{26}N_2O_4$ ⎭ in St. Ignatius' bean and in other vegetable substances.

Veratrine, $C_{32}H_{49}NO_9$. It occurs in *veratrum sabadilla,* and elsewhere.

Aconitine, $C_{33}H_{43}NO_{12}$. It occurs in the root of monkshood, *aconitum napellus.*

Solanine, $C_{52}H_{93}NO_{18}$(?). It occurs in the berries of the deadly nightshade, *solanum nigrum,* and in many parts of different *solanums ;* in small quantity in even the tubers and leaves of the edible potato, *s. tuberosum.*

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